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Issued with the July Number, 1911.

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Proceedings.

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MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

SOUTHERN CALIFORNIA SECTION.

The following meetings have been held in Los Angeles by the Southern California Section, in each case preceded by an informal dinner, the attendance numbering approximately thirty at each meeting, with Laird J. Stabler as chairman.

Tuesday evening, Dec. 13, 1910, at the Hollenbeck Café.—The application for a Southern California Section of the Amer. Chem. Soc. was signed. It was decided to hold meetings regularly once a month.

Friday evening, Jan. 13, 1911, at the University Club.—D. Basil W. Alexander addressed the meeting on "Research and Publicity."

Thursday evening, Feb. 16th, at the University Club.—The following papers were read: "The Elimination of the Smoke Nuisance in Other Cities," W. K. Gaylord. "The New Los Angeles City Smoke Ordinance" (from the standpoint of the City Health Department), E. H. Miller. Discussion (from the standpoint of the manufacturer), F. S. Wade.

Thursday evening, Mar. 16th, at the University Club.—The chairman announced that the petition for a Southern California Section of the Am. Chem. Society had been granted, and appointed W. K. Gaylord and Frank H. Merrill to constitute a Nominating Committee for officers of the new section.

Walter A. Schmidt addressed the meeting on "The Electrical Precipitation Processes for Collection of Smelter Fumes, Cement Dust, etc." (experimentally demonstrated).

Thursday evening, April 27th, at the University Club.—The Nominating Committee reported as follows: *President*, Laird J. Stabler; *Vice-President*, Henry L. Payne; *Secretary-Treasurer*, B. A. Olshausen; *Councilor*, D. Basil W. Alexander.

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The secretary was instructed to cast the ballot for the above.

Plans for future proceedings of the Section were then discussed and formulated.

B. A. OLSHAUSEN, *Secretary.*

CINCINNATI SECTION.

The 169th regular meeting was held on Wednesday evening, May 10th, at Ohio Mechanics' Institute.

The following papers were presented: "The Sewage Disposal Problem of Cincinnati and Vicinity," by J. W. Ellms. "A Quick and Accurate Method for the Analysis of White Metals," by J. C. Beneker.

ALFRED SMITH, *Recording Secretary.*

CHICAGO SECTION.

A meeting of the Section was held at the Congress Hotel on May 12th for the special purpose of awarding to Professor Svante Arrhenius the Willard Gibbs Medal, founded by William A. Converse.

The opening remarks were made by President Harry Pratt Judson, of the University of Chicago, chiefly in regard to the interchange of professional men between our schools and colleges and those abroad. His remarks were followed by an address by Mr. Harry A. Wheeler, President, Chicago Association of Commerce, on "Commerce and Science." Mr. S. T. Mather spoke on the history of the Willard Gibbs Medal and the motives which prompted its endowment. The Willard Gibbs Medal was then presented to Dr. Arrhenius by Professor Alexander Smith, President of the American Chemical Society. Professor Arrhenius delivered the Willard Gibbs address, which consisted chiefly of a résumé of his electrolytic dissociation theory with personal reminiscences of the inside history of the conception of the theory, its presentation, the storm of conflict that arose, the confirmation which followed its presentation and its final establishment in the scientific world. 220 were present at the dinner and 245 at the meeting.

D. K. FRENCH, *Secretary.*

LOUISVILLE SECTION.

The May meeting was held at Lexington, Saturday, May 13th, the Louisville, Danville and Georgetown members being guests of the Lexington members. A reception and luncheon at the Phoenix Hotel, at noon, were followed by an inspection of the new Chemistry Building of the Kentucky State University. A very interesting and instructive lecture, on Radioactivity, was then given by the honor guest, Dr. W. A. Noyes, of the University of Illinois. An inspection of the different Departments of the University followed. About fifty members and guests were present.

KARL S. MARKENDORF, *Secretary.*

WISCONSIN SECTION.

The May meeting was held at Madison, on Wednesday, May 17th,

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at 8 P.M., in the Chemistry Building. The following addresses were given: F. C. Krauskopf on "The Action of the Oxides of Lead on Potassium Tartrate Solutions;" Alcan Hirsch on "The Preparation and Properties of Metallic Cerium."

DAVID KLEIN, *Secretary.*

PHILADELPHIA SECTION.

The regular meeting of the Section was held at the Engineers' Club, Philadelphia, May 18th. The officers elected for the ensuing year were: *Chairman*, George C. Davis; *Vice-Chairman*, W. C. Carnell; *Secretary-Treasurer*, C. S. Brinton; *Executive Committee*, Geo. D. Rosengarten, Wm. H. Bower, Joel H. Hildebrand. The program consisted of an illustrated lecture by Dr. A. M. Comey, Chief of the Eastern Experimental Laboratory of E. I. Du Pont de Nemours Powder Company, on "The Testing of Explosives."

C. S. BRINTON, *Secretary.*

SECTION OF WESTERN NEW YORK.

The annual banquet and election of officers took place at the Hotel Statler, May 19th. The following were elected officers of the Section for the coming year: *President*, W. H. Watkins; *First Vice-President*, A. P. Sy; *Second Vice-President*, J. Klein; *Councilor*, F. A. J. Fitzgerald; *Treasurer*, R. E. Fowler; *Secretary*, W. Wallace; *Members of Executive Committee*, A. H. Hooker, A. Halland, J. F. Schoellkopf, Jr.

The treasurer presented his report for the year. After an address by the president, several short pseudo-chemical papers were read and other entertainments given by the members of the Section.

W. WALLACE, *Secretary.*

LOUISIANA SECTION.

The fiftieth meeting was held at the Board of Trade Room, New Orleans, Friday, May 19th, at 8 P.M. The paper of the evening was "Theory of the Polariscope and Refractometer," by Theodor Markovits, followed by five-minute discussions on chemical topics.

The 51st meeting was held on Friday, June 16th, at 6.30 P.M., at the Old Hickory Restaurant. This was the Annual Dinner and Round Table Meeting, with "Chemical Experiences" as the topic of the evening.

GEO. B. TAYLOR, *Secretary.*

NASHVILLE SECTION.

The annual meeting was held on May 19th, in Furman Hall, of Vanderbilt University. All of the officers were reelected as follows: *Chairman*, W. L. Dudley; *Vice-Chairman*, J. I. D. Hinds; *Secretary-Treasurer*, L. J. Desha; *Councilor*, R. W. Balcom.

The speaker of the evening having been suddenly called away from the State, no regular program was rendered and the Section adjourned until October.

L. JUNIUS DESHA, *Secretary.*

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GEORGIA SECTION.

The Georgia Section held its May meeting in the rooms of the Mechanical and Manufacturers Club, Atlanta, Saturday evening, May 20th. This was the most enthusiastic meeting in the history of the Section, both in numbers and in interest. A dinner was given in honor of Dr. Frank K. Cameron, who afterwards spoke on "The Theoretical Basis of Fertilizers."

J. S. BROGDON, *Secretary.*

KANSAS CITY SECTION.

Dr. Alexander Smith, President of the American Chemical Society, lectured to the members of the Kansas City Section and their friends, at the Chemistry Building, University of Kansas, at three o'clock, Saturday afternoon, May 20th.

The first lecture was on the "Teaching of Chemistry." After an intermission, Dr. Smith gave another lecture on "Some Recent Work on Vapor Pressure." Dinner was served after the last lecture.

E. A. WHITE, *Secretary.*

UNIVERSITY OF MICHIGAN SECTION.

The Section met in the Chemical Building, May 25th. Attendance, 35. The following papers were presented: "A Survey of Quenched Steels," illustrated, by K. W. Zimmerchied. "The Mechanism and Accuracy of the Volhard Titration for Copper," by W. G. Smeaton.

W. G. SMEATON, *Secretary.*

RHODE ISLAND SECTION.

The regular meeting was held at the University Club, on Thursday evening, May 25th, preceded by dinner, at 7 o'clock.

The speaker of the evening was Mr. I. S. Hartman, B.S., of The Thermal Syndicate, Ltd., who spoke on "Apparatus of Fused Silica. Its Preparation, Chemical and Physical Properties, and Uses."

ALBERT W. CLAFLIN, *Secretary.*

MILWAUKEE SECTION.

The Section held its regular meeting on Friday evening, May 26th. Mr. George N. Prentiss, chemist of the Chicago, Milwaukee & St. Paul Ry., gave a talk on "Boiler Room Chemistry." There was a lively discussion, in which the best points in modern steam engineering practice were brought out.

BEN L. SALOMON, *Secretary.*

NEBRASKA SECTION.

The sixty-fourth regular meeting—being the fourth annual Omaha meeting—of the Nebraska Section was held in Omaha on Friday, May 26th.

Dr. Alexander Smith, President of the American Chemical Society, was the guest of the Section.

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At 4 P.M., a visit was made to the laboratories of the Omaha High School, after which a reception was given Dr. Smith by the Science Teachers.

At 4.30 P.M., Dr. Smith gave an address, "Science in the High School."

The Section gathered at the Hotel Rome at 6 P.M. for a reception to Dr. Smith and this was followed by a dinner at 6.30 P.M.

At 8 P.M., Dr. Smith addressed the Section on "Vapor Pressures and Dissociation Pressures."

On Saturday, May 27th, Dr. Smith visited the University of Nebraska, in Lincoln. At noon, a luncheon was given by the Faculty of the University in honor of Dr. Smith, at the New Lindell Hotel. Following the luncheon, Dr. Smith spoke extemporaneously for a few minutes on methods of teaching Science.

In the evening at 8 P.M., in the Lecture room of the Brace Laboratory, Dr. Smith gave his lecture, "The Balance Sheet of Science."

C. J. FRANKFORTER, *Secretary.*

CORNELL SECTION.

The last meeting of the year was held Tuesday, May 30th, in Morse Hall, at 8.30 P.M. The following ten-minute papers were given: "The Phthaloximes and Some of Their Derivatives," D. S. Pratt. "Electrolytic Reduction of Nitro-benzene without a Diaphragm," E. F. Farnau. "Octochlorindigo and Some Derivatives of Tetrachlorphthalic Acid and Tetrachloranthranilic Acid," E. H. Nichols. "Colloidal Suspensions," T. R. Briggs. "Aluminum Anodes in Liquid Ammonia Solutions of Ammonium Trinitride," M. J. Brown.

The following officers were elected for the coming year: *President*, L. J. Cross; *Vice-President*, R. P. Anderson; *Secretary-Treasurer*, J. C. Andrews; *Executive Committee*, the above and W. R. Orndorff, H. W. Redfield, H. E. Riegger.

J. C. ANDREWS, *Secretary.*

NEW YORK SECTION.

The ninth regular meeting of the session of 1910–11 was held in Rumford Hall on June 9th, Prof. Chas. Baskerville in the chair. The following papers were presented: Edward C. Kendall, "Determination of Copper: A Modification of the Iodine Method." A. C. Langmuir, "Report of the Sub-Committee on Glycerine Analysis." Allen Rogers, "Consistency of Paint by the Stormer Viscosimeter." Maximilian Toch, "Fish-Oil as a Paint Vehicle." Morris Loeb and S. R. Morey, "Studies on the Reduction of Ferric and Ceric Salts" (read by title). A. B. Lamb and J. W. Marden, "An Equilibrium in Cobaltamines." Chas. Baskerville and W. A. Hamor, "Chemistry of Anaesthetics: IV. Chloroform."

C. M. JOYCE, *Secretary.*

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INDIANA SECTION.

The Section met at the office of the State Food and Drug Laboratory, Indianapolis, on Friday evening, June 9th, at 8 o'clock, with about 25 members present.

The following papers were read: "A Method for Lead and Its Electrolytic Separation from Copper," G. Patterson, Jr. "Van't Hoff's Influence on the Development of Chemistry," A. R. Middleton.

A. D. THORBURN, *Secretary.*

DECEASED MEMBERS.

Stephen T. Ernst, Jersey City, N. J.
Herbert Hollick, May 3, 1911, Camden, N. J.
N. W. Lord, May 23, 1911, Columbus, Ohio.
Cameron Piggot, Sewanee, Tenn.
Edward B. Voorhees, New Brunswick, N. J.

Jacobus Henricus van't Hoff.

Jacobus Henricus van't Hoff was born in Rotterdam, on August 30, 1852. In spite of not having studied Latin he was admitted to the University of Leyden in 1871. He passed the first examination in 1872, after which he worked a while with Kekulé at Bonn and with Würtz at Paris. Returning to Holland, van't Hoff took his doctor's degree in 1874 at Utrecht under Mulder. In 1876, van't Hoff was appointed instructor in physics at the veterinary college in Utrecht; in the following year he went to Amsterdam as a chemist; and in 1878 he was appointed professor of chemistry at the University of Amsterdam. When the chair of physical chemistry was founded at Leipzig, about 1887, it was offered to van't Hoff, who declined the call, whereupon the authorities appointed Ostwald. In 1893, van't Hoff was asked to go to Berlin as professor of physics but declined. In 1894, the University of Berlin and the Prussian Academy made him a joint offer of an exceptional nature. In consequence, van't Hoff moved to Berlin where he spent the rest of his life.

The reputation of van't Hoff is that of a great thinker, of a man who has taught people to look at facts in a new way. Although a good experimenter, it was his imaginative power and not his manipulative skill which raised him head and shoulders above the chemists of his time. In his whole life he never made what would be called a very accurate measurement and he never cared to. I remember his saying to me eighteen years ago: "How fortunate it is that there are people who will do that sort of work for us!" While extreme accuracy is a gift to be admired, it is a greater thing to have changed the whole development of chemistry, not once but several times.

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In 1874, van't Hoff published a paper on three-dimensional structure formulas, and in 1877, a much elaborated German translation appeared. The theory of the tetrahedral nature of the carbon valences with its corollary of the asymmetric carbon atom enabled people to account for such cases of isomerism as fumaric and maleic acids and also to account for the optical properties of the tartaric acids, etc. Nevertheless, the new doctrine was not received enthusiastically, and if it had not been for the active support of Wislicenus, it is quite possible that this important generalization might not have been accepted as a working hypothesis for a great many years. Even as it was, I know of lectures on organic chemistry delivered late in the 80's in which van't Hoff's theory was alluded to as a bit of reckless speculation. With increasing knowledge of organic compounds, there has come increased respect for van't Hoff's generalization, and the only question nowadays is as to the number of elements to which it may be profitable to apply a similar reasoning.

After such a start, most men would have worked at stereochemical problems for the rest of their lives; but van't Hoff's imaginative genius was always on the lookout for new problems to solve. The next developments, and all the subsequent ones, were in the field of what is now called physical chemistry. Van't Hoff rediscovered the mass law and put the formulas for reaction velocity on a better basis than had previously been the case. The later work of A. A. Noyes showed that van't Hoff's method of determining the order of a reaction was less liable to error than the apparently simpler one of seeing which formula best represents the whole course of the reaction.

It was a natural transition from the study of equilibrium at constant temperature to the study of the change of equilibrium with changing temperature. We owe to van't Hoff the formula establishing the relation between the heat of reaction and the change of equilibrium constant with changing temperature. Van't Hoff also worked out the relation between chemical affinity and electrical energy independently of, though subsequent to, the work of Gibbs. For the special case of the inversion point, van't Hoff obtained a relation between chemical energy and heat effect which coincided with the more general result previously obtained by Helmholtz. For a while it looked as though the work on electromotive forces was not going to produce its proper effect; but the experiments of Cohen and of Bredig have shown people the importance of van't Hoff's views. All our quantitative work on chemical affinity is the direct outgrowth of van't Hoff's studies on this subject.

To this same period we owe the theory of condensed systems, a theory which had not the scope of the phase rule but which served for a while as an excellent guide through the mazes of heterogeneous equilibrium.

A study of Pfeffer's experiments on osmotic pressure led van't Hoff,

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in 1886, to his osmotic pressure theory of solutions, which enabled him to deduce equations for the relation between concentration and change of vapor pressure which were practically equivalent to those found empirically by Raoult. This was a tremendous step in advance. The scope of the theory was increased enormously by Arrhenius's theory of electrolytic dissociation. The two theories gave rise to Nernst's theory of the voltaic cell. With these three theories as a starting point, Ostwald's marvelous power of presenting facts carried everything before it and all three theories are now part of the accepted doctrine all over the world. The opposition to them now deals really with questions of detail and would prove more effective if that were realized. It is interesting to note that van't Hoff's original deduction of the so-called van't Hoff-Raoult formula is still the best, in that it does not obscure the assumptions involved.

After moving to Berlin, van't Hoff began the study of the Stassfurt salt deposits and here we find a trait which is characteristic of the man. In previous work, van't Hoff had made use of his own theory of condensed systems in preference to using the phase rule with which he had become familiar later in life through the work of Roozeboom. This was legitimate and natural for the simpler cases; but the theory of condensed systems was quite inadequate to grapple with such a problem as that involved in the study of the Stassfurt salt deposits. Consequently, van't Hoff discarded it and his brilliant application of the phase rule did much to awaken people to the possibilities of this instrument of research. It is also not too much to say that this stupendous investigation of van't Hoff's was one step in the revolutionizing of the study of geology. The Geophysical Laboratory, at Washington, is doing for igneous rocks what van't Hoff did for Stassfurt salt deposits. Had it not been for Roozeboom, the work of the Geophysical Laboratory certainly could not have been done. Had it not been for van't Hoff, the work of the Geophysical Laboratory probably would not have been done.

At the time of his death, van't Hoff was engaged on an entirely new problem fully equal in importance to anything that he had solved before. He was studying the problem of the living plant, the chemistry of life as opposed to the chemistry of the beaker. Since van't Hoff was carried off in the full height of his powers, there is no reason to doubt that we should have had another series of epoch-making results, if he could have succeeded in throwing off the tuberculosis.

With such a career it is almost superfluous to say that van't Hoff was the recipient of many honors. It is worth noting, however, that he received the first Nobel prize in Chemistry and that the reward was universally recognized as the only one that could be made.

The man himself was on a par with his work. Van't Hoff was one of

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the most delightful and charming men imaginable. All who knew him loved him. Kipling's lines to Wolcott Balestier might well have been written of van't Hoff.

"He scarce had need to doff his pride or slough the dross of earth—
E'en as he trod that day to God, so walked he from his birth,
In simpleness and gentleness and honour and clean mirth.

"So cup to lip in fellowship they gave him welcome high
And made him place at the banquet board—the Strong Men ranged thereby,
Who had done his work and held his peace and had no fear to die.

"Beyond the loom of the last lone star, through open darkness hurled,
Further than rebel comet dared or living star-swarm swirled,
Sits he with those that praise our God for that they served his World."

WILDER D. BANCROFT.

VAN'T HOFF MEMORIAL COMMITTEE.

A van't Hoff Memorial Committee has been formed at Amsterdam, with Professor H. A. Lorentz, of Leiden, as Honorary President, Professor A. F. Holleman, of the University of Amsterdam, as Acting President, and Dr. E. H. Büchner, of Nieuwe Prinsengracht 126, Amsterdam, as Secretary. The purposes of the committee are to erect a memorial in honor of Professor van't Hoff and to form a van't Hoff Institution for the advancement of chemical research. It is hoped that American chemists will contribute to the movement. Any remittances should be sent to the secretary named above.

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THE JOURNAL

OF THE

American Chemical Society

THE SPECIFIC GRAVITIES OF THE ELEMENTS CONSIDERED IN THEIR RELATION TO THE PERIODIC SYSTEM.[1]

PART I. ATOMIC VOLUMES.

BY ARTHUR JOHN HOPKINS.

Received April 19, 1911.

Introductory.

The periodic system of the elements, as established by the separate papers of Mendeléeff and Meyer in 1869, is based upon three important arguments:

1. Recurrence of chemical properties.
2. Similarities of valence.
3. Recurrence of physical properties.

In regard to the first argument, the fact that chemical properties are shared by certain elements in groups had been already noted long before 1869, but as a pioneer it had proved too weak an argument to suggest a complete system of the elements in families. The second appeal was of greater influence. The gradual awakening in the minds of chemists to the significance of the term valence through the work of Frankland, Kekulé, Couper, Wurtz, LeBel and van't Hoff, and of Erlenmeyer, did much to guide the thoughts of critics towards the final acceptance of the completed periodic system. Against this, however, nothing has acted so strongly in the way of a counter-argument as the necessity of accepting with valence the accompanying conception of variable valence. Thus the second appeal lost much of its persuasive force. Historically, no one contribution has been of such lasting influence as the third of the above arguments—the recurrence of physical

[1] The essentials of this paper were first presented before the Science Club of Amherst in December, 1907, and the paper was then presented in abstract before the American Chemical Society at the New Haven meeting in July, 1908.

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properties—especially as developed by Meyer's curve of atomic volumes. The fact that physical properties, as well as chemical, could be shown to vary periodically with the atomic weights was early accepted as a strong argument in favor of the fundamental periodicity, and the forty years which have followed have only confirmed chemists in this favorable attitude. The first test, therefore, to which any system of atomic weights has been, or is likely to be subjected, is that of its agreement with or explanation of this historically important curve of atomic volumes.

It is proposed in the present paper to discuss the real meaning of this relationship—atomic volumes; and in the second paper following, the bearing of the conclusions in the first paper upon the form of the periodic system.

Significance of Atomic Volumes.

It is remarkable, considering the fundamental importance of the curve of atomic volumes, that no careful analysis of it has ever been published. The simple interpretation, given in the succeeding pages, may have been previously grasped by students, may even have been assumed by Meyer;[1] but it is evident that the real significance of the curve has not been clear to the writers succeeding him. It will not be amiss, therefore, to express in as few words as possible some fundamental thoughts beyond the bare statement, so often repeated, of the remarkable fact of the existence of the curve.

If we examine Chart I, we find that Meyer has charted atomic volumes on the one axis and atomic weights on the other (see page 1007).

There is a direct relation between these two values for we have

$$\text{Atomic volumes} = \frac{\text{atomic weight}}{\text{specific gravity}}, \text{ or}$$

$$\text{Atomic volume} = \text{atomic weight} \times \text{specific volume},$$

and when we place

$$\text{Atomic weight} \times \text{specific volume}$$

on the axis of ordinates, and

$$\text{Atomic weight}$$

on the axis of abscissas, we have a curve every point of which has an x and y such that the ratio y/x = specific volume.

Meyer's curve owes its periodicity to the variation in specific volumes. For the emphasis which he desired—to establish the importance of atomic weights—he was right in drawing the curve as he did, complicated by the atomic weights. Yet because of this desire he has allowed this complication to cloud an important simple thought which may be stated as follows:

[1] Meyer makes nowhere a statement to this effect and his argument was perhaps left clearer without this complication.

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Given the orderly succession of the atomic weights,

The periodic character of the curve of atomic volumes is due to specific gravity alone.

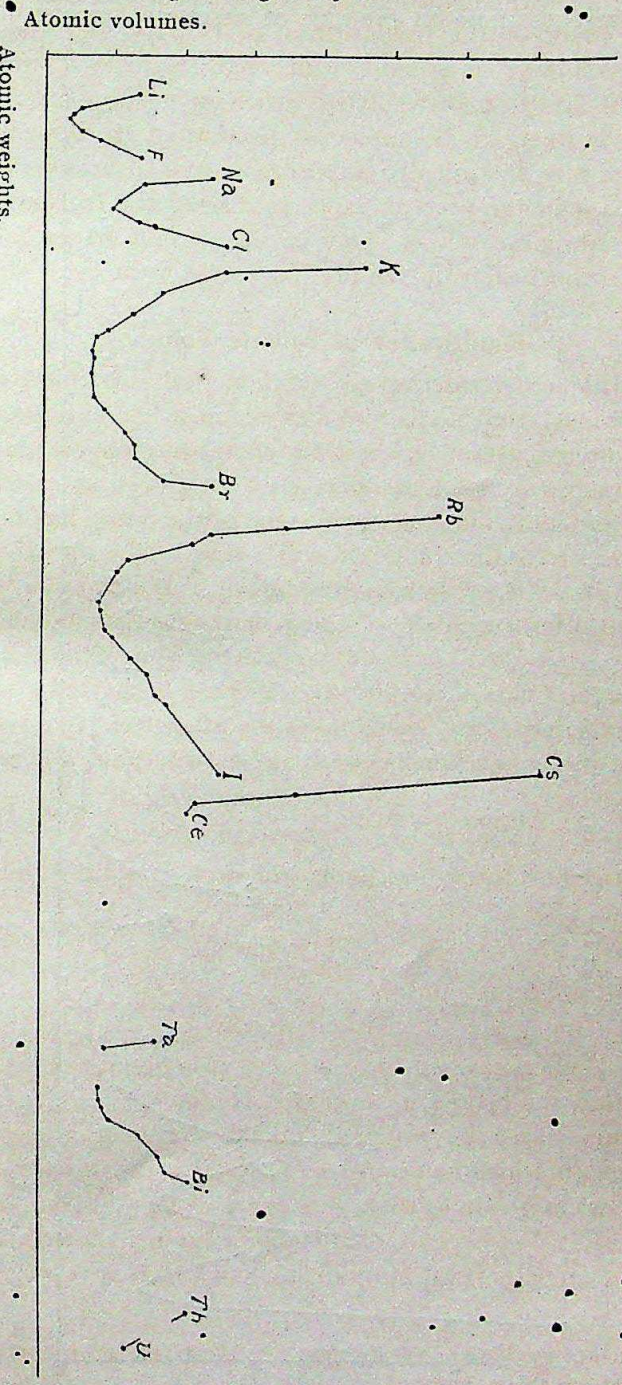

Chart I. Meyer.

"The atomic volumes are periodic functions of the atomic weights."

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Another proof of this same fact may be reached by the method of elimination; for if in plotting $\frac{\text{atomic weights}}{\text{specific gravities}}$ on the axis of ordinates and atomic weights alone on the axis of abscissas, we consider the item

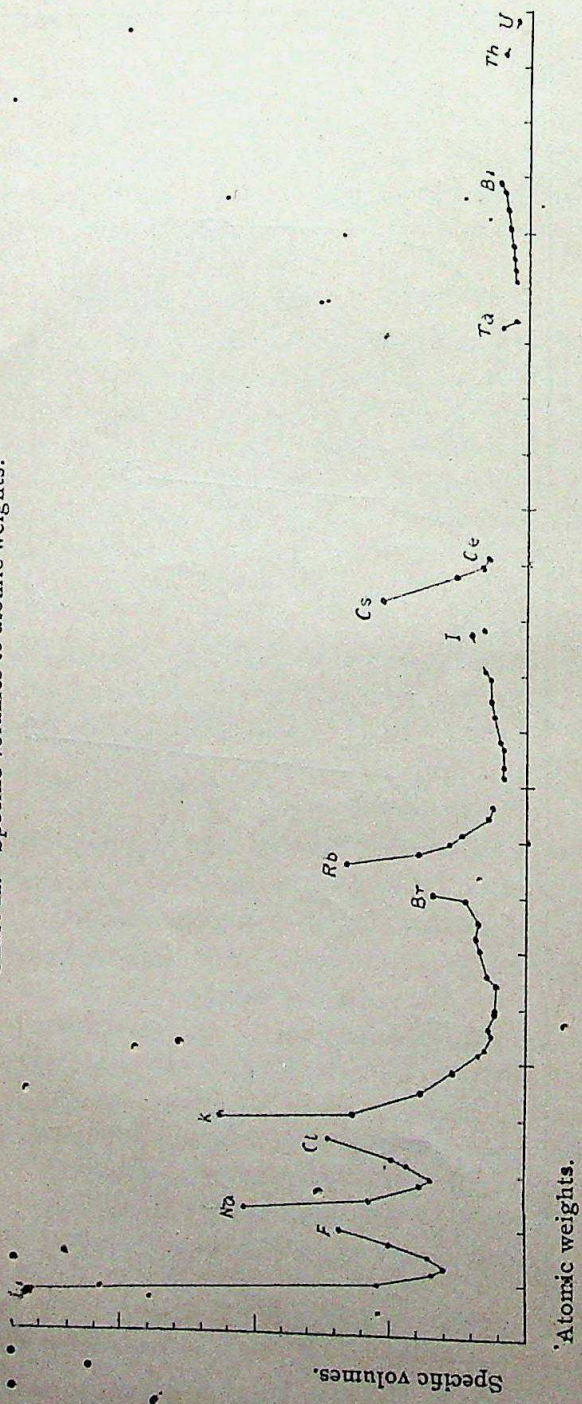

Chart II. Specific volumes to atomic weights.

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specific gravities to remain a constant, periodicity entirely disappears, for we are now plotting atomic weights on the one axis against atomic weights on the other axis; and the curve is a right line.

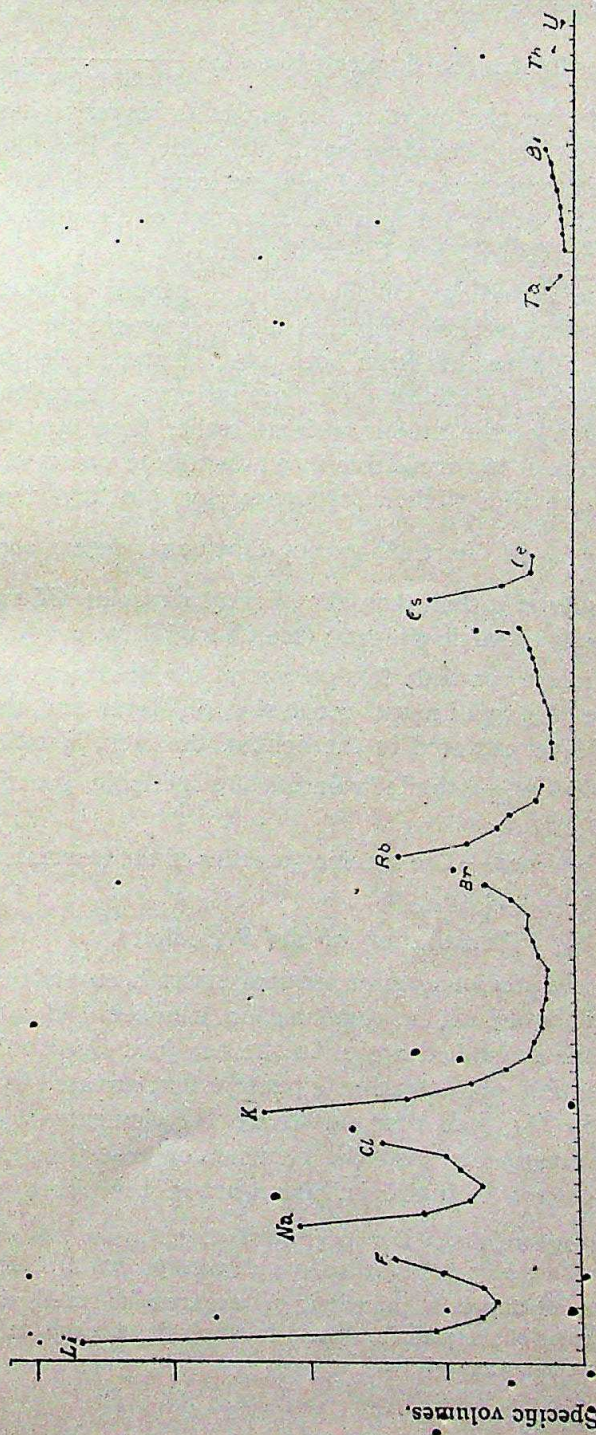

Chart III. Specific volumes to equal spaces.

Equal spaces.

Specific gravities are periodic functions of the atomic weights.

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It is evident therefore that the periodic character of this curve is due wholly to the one item, specific gravity.[1] In the following chart, in the place of the expression $\frac{\text{atomic weight}}{\text{specific gravity}}$ or atomic volume, is substituted on the axis of ordinates the simpler expression $\frac{1}{\text{specific gravity}}$ or specific volume. Otherwise, the chart is the same as Meyer's. As we should expect from what has been developed, although the irregularly increasing value of the atomic weights is eliminated from the one axis (ordinates) and not from the other, the general character of the periodicity is the same as shown on Chart I (see Chart II, p. 1008).

But since the periodicity of the curve of atomic volumes has been shown to be due to specific gravities alone, it would seem more exact to eliminate atomic weights from both axes. Later in this paper it will be shown that the periodicity under discussion is dependent upon the orderly succession of the atomic weights rather than upon their actual values. Therefore it is permissible to eliminate the values of the atomic weights while retaining their sequence by plotting the expression $\frac{1}{\text{specific gravity}}$, as in Chart II, except that equal spaces are allowed on the axis of abscissas rather than the slightly irregular differences in the values of successive atomic weights[2] (see Chart III, p. 1009).

We may therefore conclude this portion of the discussion by two statements, the one the well-known conclusion of Meyer and the other the expression of Meyer restated in the light of the facts just developed.

Meyer's Statement.—Atomic volumes are periodic functions of the atomic weights.

The Same Simplified.—The specific gravities of the elements are periodic functions of the atomic weights.

Explanation of the Periodicity.

Although, in the previous section, an analysis has been made of the periodic curve of atomic volumes, no explanation has been advanced for the periodicity in the original curve or in the one just given. On searching for such explanation, our attention is perhaps first arrested by the valence relation, *i. e.*, by the fact that on Chart III elements of low specific gravity (at the crests) are also the elements of lowest valence and that as the valence towards hydrogen increases in the short periods from

[1] It is clear, therefore, that if our judgment is based upon this curve alone the much discussed and much quoted function, atomic volume, has little significance.

[2] This has the advantage of presenting an arrangement strictly in accord with the usual arrangement of the periodic system in which the elements are allotted equal spaces on the chart (see Chart XI).

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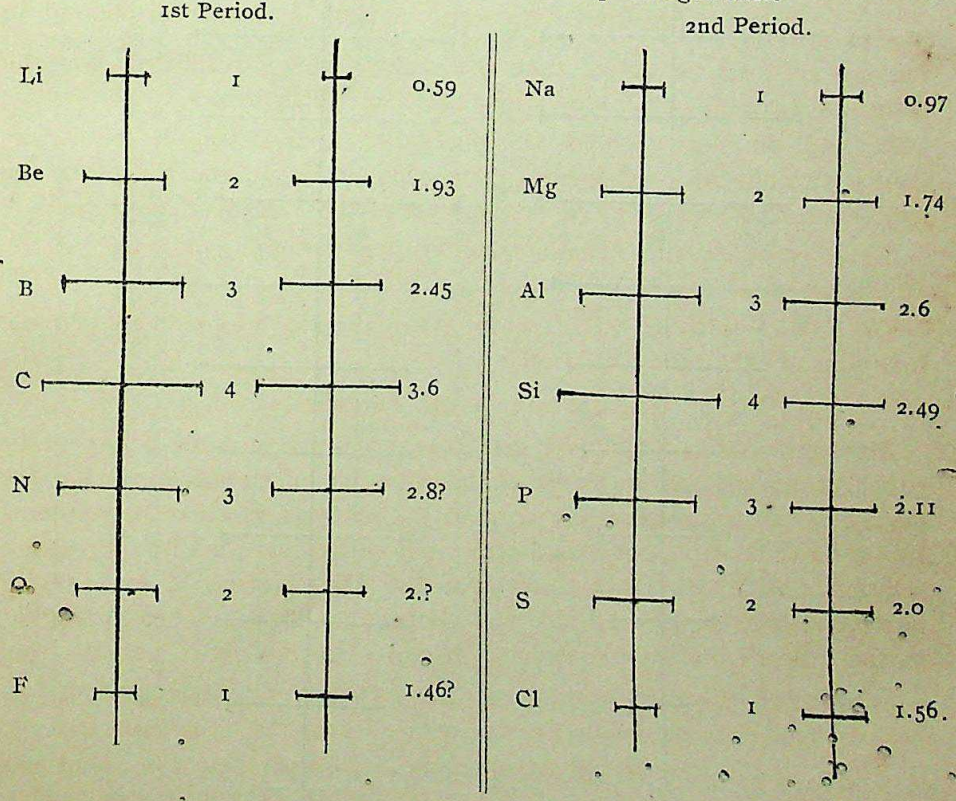
one to four and then falls to one (or zero), exactly so does the specific gravity vary, so that we may be permitted to number the positions of the elements in the short periods in the same sequence as that indicated by both valence and specific gravity. The position-numbers would then read

1—2—3—4—3—2—1—0

4789

With this numbering established for reference, we may find the influence which position-number may be said to have on specific gravity. It is a remarkable fact that in the case of each element in the short periods the ratio of the position-number (which is established only by the succession of atomic weights in the period) to the valence of the element towards hydrogen is a constant; and again to the specific gravity is (nearly) a constant. This similarity in sequence may be shown by the following parallel columns in which the lengths of the lines show for the successive elements in the two short periods: first the position-number of valence; and second the specific gravity.

Valence and position-numbers; and specific gravities.



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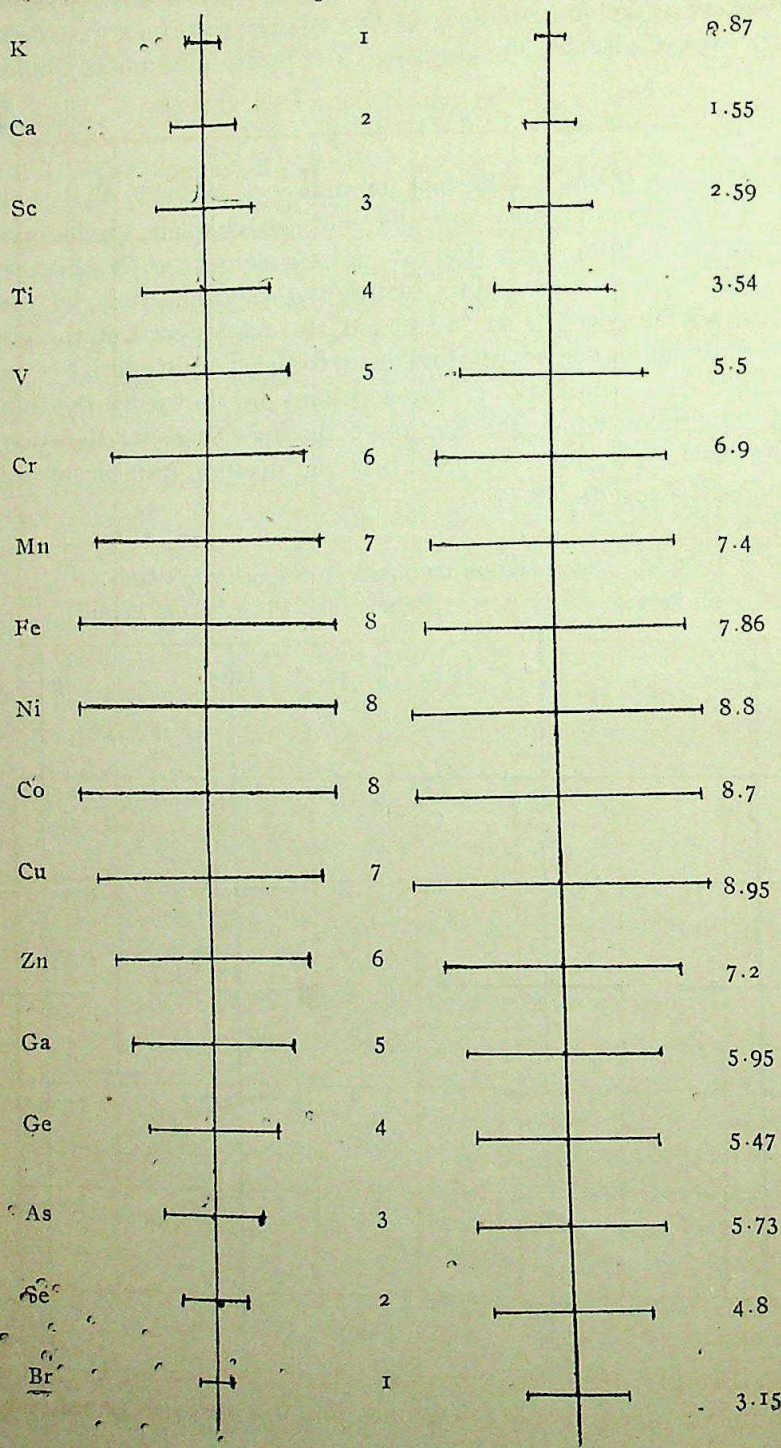
Valence and Position-numbers; and Specific Gravities.

3rd Period.



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This may be better shown by plotting on one chart two curves, one of position-number and one of specific gravity. For the first two periods, the curves are as follows:

Chart IV (1).

Curves of position number and specific gravity.

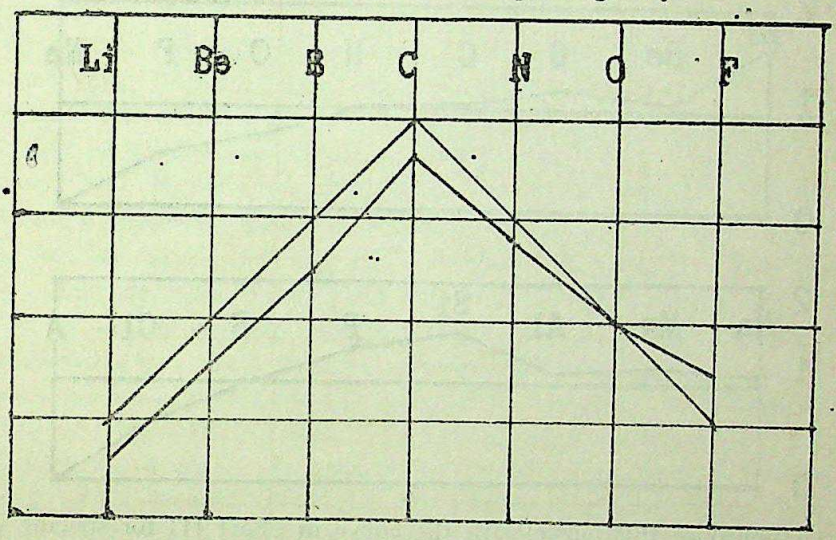
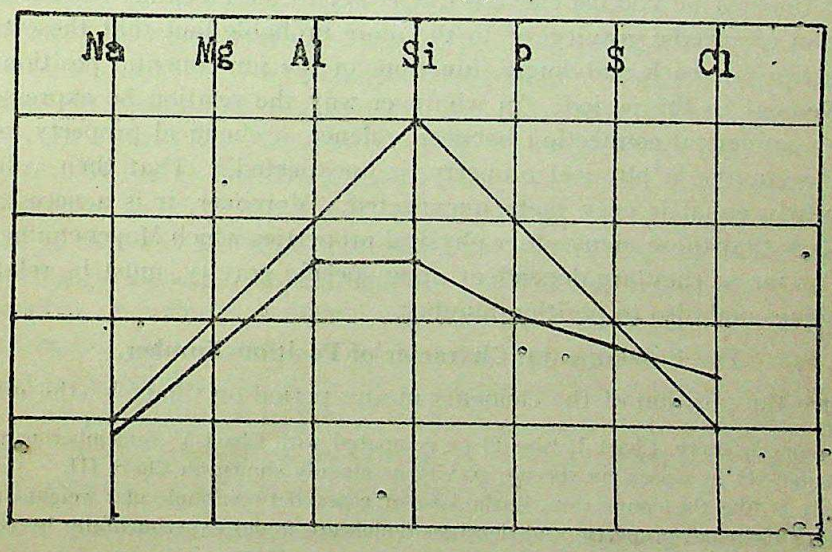


Chart IV (2).



If further we plot these two curves as a ratio, by dividing in each case position-number by specific gravity, and plot this ratio to equal spaces,

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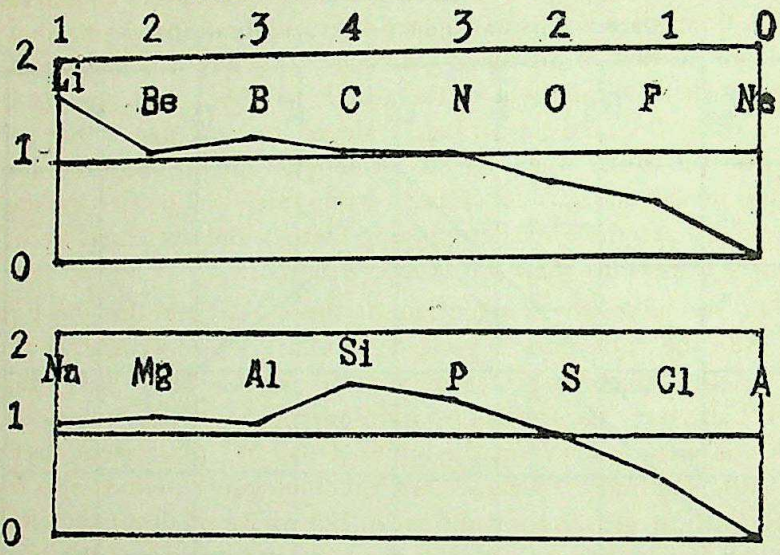
the marked periodicity of Meyer's curve has disappeared[1] and the resulting ratio curve is found to be nearly horizontal:

Chart V.
Position number times specific volume.



If we compare this curve with the curve in Chart III for specific volumes (choosing this in order that both curves compared may be plotted to equal spaces) we are led to the conclusion that the remarkable flattening of the specific volume curve is due either to the fact that valence is a function of specific gravity, or to the more probable fact that these two properties are, each and singly, functions of the fundamental position of the element in the period. In whatever way the relation be expressed, even a numerical connection between valence, a chemical property, and specific gravity, a physical property, is unexpected.[2] That their values are nearly equal is even more unexpected. Moreover, it is a necessary corollary that those many other physical properties which Meyer enumerated,[3] as far as they are dependent upon specific gravity, must be related to valence and also to position-number.

The Fundamental Character of Position-Number.

Since the position of the elements in any period on Chart V (the num-

[1] Meyer's curve, Chart I, should be compared with Chart V, remembering that the periodicity is caused by specific gravity as already shown on Chart III.

[2] It is like the connection, in the case of gases, between molecular weights, and atomic or chemical property, and densities which are found experimentally by comparing physical volumes.

[3] Besides valence and atomic volume, Meyer discusses states of aggregation, ductility, malleability, volatility, electrochemical behavior, expansion by heat, refraction of light, conductivities of heat and light and magnetic properties.

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bers of which may be taken as decreasing from a central maximum) are fixed, being determined by the succession of the atomic weights, I regard position in the period as the fundamental property; and specific gravities, valences (and all properties dependent upon these) as functions of it. At a time when it was customary to calculate properties against *mass*, Meyer took a step in advance, teaching that physical phenomena are to be regarded as functions of the atomic weights. But now, in further advance upon the above teaching of Meyer, we may assert that physical properties are to be regarded as functions of the position-numbers; and that in calculations involving certain physical properties the position-numbers are the only determining factors and are therefore in these cases more important than the atomic weights.

So far, we have given attention to the curves for the short periods only. But the ratio curves plotted on Chart V are typical of those to follow as the succeeding statements will show. They have the same general character. The ratio of position-number to specific gravity on Chart V does not vary much from the limits of 1.0 and 1.2, except that at the end it falls gradually to zero.[1] In the succeeding periods also we shall find, for each, a nearly constant ratio; but as we go down the chart, the average of the specific gravities of the elements in each of the successive periods increases faster than the increase in average atomic weights, so that this ratio becomes less. From the first period to the last it has fallen from 1.1 to 0.4. But the horizontal character of the curves appears again, in each period, as it did in the first two. We get, for all the periods, curves of the same character as those just plotted. But these may be obtained only by distinguishing between short periods and long periods, as they are distinguished in Meyer's curve, Chart I, as well as in Charts II and III. This requires in the long periods positions from one to eight rather than from one to four. In Meyer's chart, in the first two periods, both valence- and position-number rise from one to a maximum of four and fall from that maximum gradually to zero; and in the following periods the position-number and valence rise step by step to a possible "maximum of eight" and then (valence being irregular) position-number falls to zero. That the rise and fall of specific gravities keep pretty regular step with the position-numbers may be seen by the following parallel columns for the first long period, which may be taken, without further repetition, as typical of similar columns which may be easily constructed for the succeeding periods.

If we plot these values on one chart, we will continue Chart IV for the third (or first long) period as follows:

[1] Lithium alone, as far as we know, of all the elements plotted by Meyer in the whole chart (see Chart VI) occupies a position which we must regard as anomalous.

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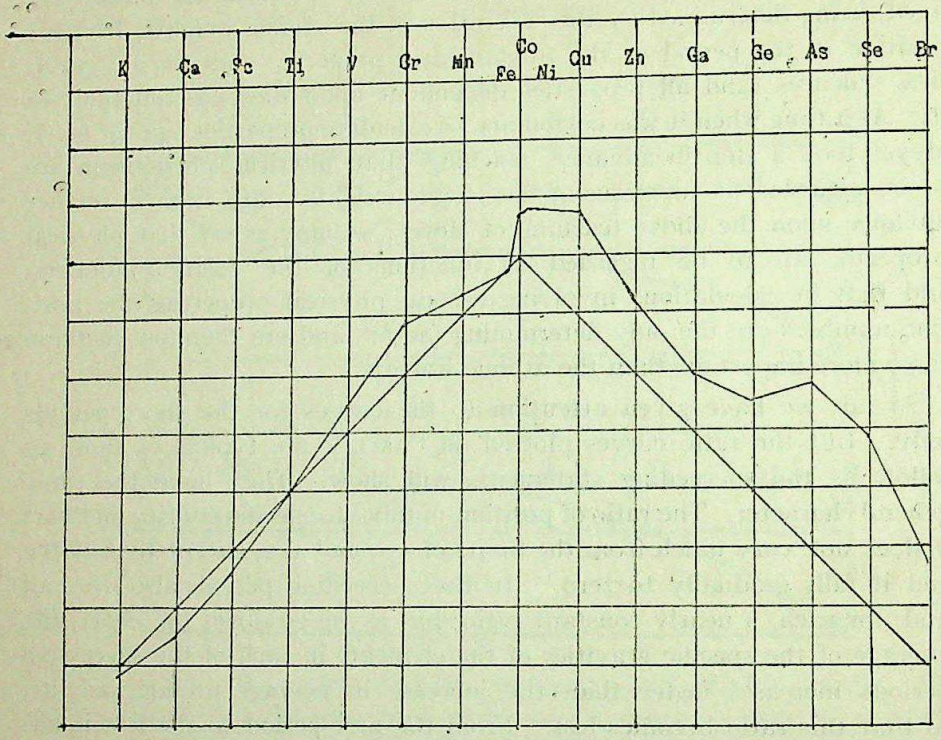
Chart IV. (3).



Continuing with the ratio curves, such as were shown on Chart V for the short periods only, we have in the following, Chart VI, for all periods, a complete exhibit of this ratio, position-number to specific gravity. Assigning, in the long periods, position-numbers from one to a maximum of eight, the character of the curves proves much the same as in the short periods—nearly horizontal but gradually falling off towards the end to zero (see Chart VI, p. 1017).

From these curves we must conclude that the position-numbers (which denote only the orderly succession of the atomic weights) change *pari passu* with the specific gravities of the elements occupying those positions. This points to a remarkable numerical relation between the position of the element in its period and its specific gravity. So simple is this that in order to calculate the position of an element in its period we have in most cases only to consider its specific gravity and take the nearest integer. For example, in the first two periods the average may be taken roughly for the ratio $\frac{\text{position-number}}{\text{specific gravity}}$ as 1.1, which means that the position-number will be in each case a little larger than the figure for specific gravity. Since the specific gravity of beryllium is 1.85, therefore its position is 2; that of boron is 2.85, therefore its position is 3; that of carbon (diamond) is 3.6, therefore its position is 4. The specific

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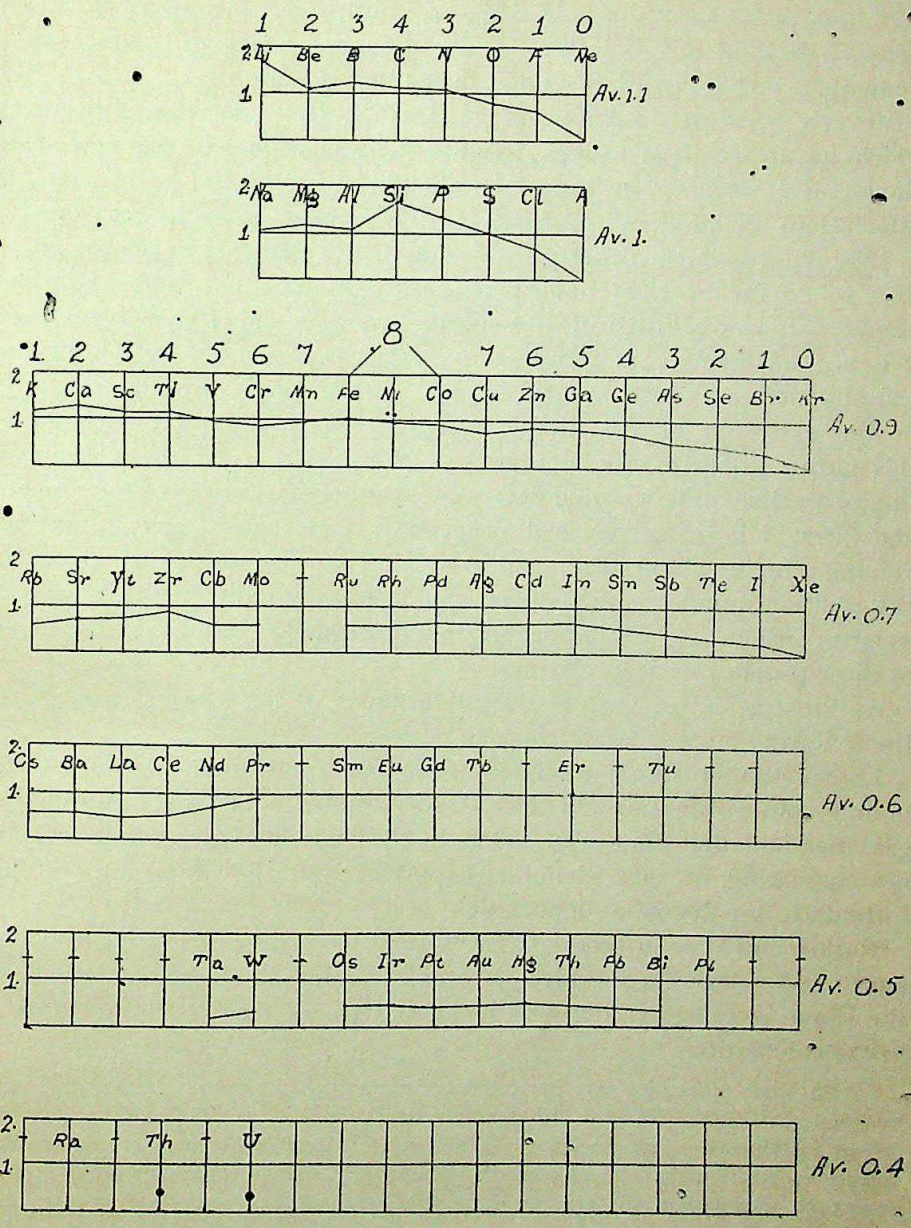
Chart VI. Position number × specific volume.



gravities of sodium, magnesium and aluminum are respectively 0.97, 1.74, and 2.60, which assigns them respectively the positions in the second period one, two and three, which we know they occupy. Conversely, from the position-number in the first long period, where the ratio is about 0.9, we may judge of iron that its specific gravity is a little less than eight. It is given as 7.86. We have thus a memory-guide

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to the specific gravities of the elements. This applies especially to the first four periods, as our knowledge of the proper arrangement of the elements beyond this as well as of the specific gravities of the rare-earth elements is not as complete as it is in the first portion.

Meyer's greatest contribution to this subject was the importance which he attached to atomic weights in calculation—in place of mass alone. But we now see that they should be introduced with care into calculations of physical properties.[1] They need enter in only so far as they determine the orderly succession of the elements in the periods—that is, so far as they determine position-numbers. Since position-numbers are nearly identical with specific gravities, and often with valences, it is not surprising that formulas for physical properties have been empirically derived which involve specific gravities only or valencies only, to the exclusion of the atomic weights. Each successive formula of this nature confirms the argument of this paper, *i. e.*, that the position of an element in a period determines the specific gravity of the element and through it other physical properties; and that in calculations involving atomic volumes the atomic weights may be neglected, provided the position-number is introduced, for it is only indirectly that atomic weights, which are all-important in chemical calculations, are involved in these purely physical relations.

As illustrations of such empirical formulas as have been referred to, the following have recently come to notice:

Longinescu in 1901[2] published a formula for the calculation of the boiling points of liquids and the melting points of solids, involving specific gravities and the number of atoms in the molecule (the atomic weights not appearing in the calculation), and showed the application of his formula to the degree of dissociation.

Barlow and Pope in 1906,[3] in their theory of valence and crystallography, have used valence in the place of atomic volume in their calculations of the shape of crystals; and here again the atomic weights do not appear in the calculations.[4]

[1] Physical properties may involve specific gravities simply; or these complicated by internal motion. We may also have physical properties in which specific gravities do not function (*e. g.*, specific heat). Wherever this item enters at all, the figures for valence or position may be substituted without any serious change of ratio. As an important illustration of this, we have the equivalent (= At. wt./valence) and atomic volume (= At. wt./sp. gr.)—one a purely chemical quantity and the other so often used with purely physical significance. Yet they are arithmetically nearly identical!

[2] Annales scientifiques de l'universite de Jasy.

[3] *J. Chem. Soc.*, p. 1675.

[4] Barlow and Pope seem however to advance a theory the reverse of that of Meyer's and of that advanced in this paper. According to their paper valence and atomic volume vary together while in the Meyer curve the valence is a minimum when the atomic volume is a maximum; and in this paper, when specific volume is a maximum.

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Richards and his students published, in 1907,[1] a paper on the compressibilities of the elements and their periodic relations in which he showed a periodic curve, similar to the curve of atomic volumes, plotted by calculating compressibilities against atomic weights. This paper will be discussed in Part II.

Verschoyle, in 1908,[2] in an article on the periodic system, insists on the influence of specific gravity on the position of elements in the system.

Traube, in 1909,[3] contends that atomic volumes (*i. e.*, specific gravities) must be used in the place of atomic weights in periodic relationships.

Conclusion.

In Part I of this paper, the author has attempted to make clear:

1. That the following values are interchangeable: for atomic volume, the ratio of atomic weight to valence (equivalent), the ratio of atomic weight to position-number; for specific volume, the reciprocal of valence or of position-number; for specific gravity, valence or position-number.

2. That in all relations involving atomic volume we may eliminate atomic weight and then substitute the reciprocals of specific gravity, valence or position-number.

3. That the periodicity of the atomic volumes curve is not directly dependent upon the item atomic weights, as might be inferred from the writings of Meyer, but is due to the physical property specific gravity.

4. That among the numerically closely related figures for specific gravity, valence and position-number, the latter may be considered fundamental since the orderly succession of the atomic weights is fundamental.

Part II.—The Form of the Periodic System.

Historical.

From the date of the first publication of the periodic system by the authors, many suggestions have appeared tending to modify the fundamental arrangement. The recent years which include the discovery of the rare-earth elements and that of the members of the argon family have been productive of valuable papers bearing upon the position of these elements in the system and upon the proper form of the table. Suggestions and discussions of this nature, which will repay careful study, are to be found in the work of Thomsen in 1895,[4] Steele in 1901,[5] Staigmuller[6] and Biltz[7] and Braunes[8] and Rudorf in 1902,[9] Gooch in his

[1] *Car. Pub. Inst.*, 76.
[2] *Chem. News*, 97, 226.
[3] *Physik. Z.*, 10, 667.
[4] *Z. anorg. Chem.*, 1895, 190 and 293.
[5] *Chem. News*, 1901, 245.
[6] *Z. physik. Chem.*, 1902, 245.
[7] *Ber.*, 1902, 562.
[8] *Z. anorg. Chem.*, 1902, 1.
[9] *Ibid.*, 1902, 107.

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recent text,[1] Benedicks in 1904,[2] Abegg in 1904 and 1905,[3] Werner in 1905,[4] Verschoyle in 1908,[5] Egerton in 1909[6] and of Loring in 1909.[7]

Those proposed forms which disrupt the short periods, leaving a necessary blank space in the middle, *e. g.*, between carbon and nitrogen and between silicon and phosphorus, may be dismissed from consideration, for blank spaces always stand in other portions of the chart for possible elements, and the differences in the numerical values of the atomic weights of the elements so separated is too small to allow of this possibility, as Abegg has already stated.

Recognition of Short and Long Periods.

The arrangement which can alone be satisfactory is one which is concise and in which allowance is made for short and long periods. The necessity for this latter requirement was not so realized by Mendeléeff as to modify his periodic arrangement. Referring to Part I, it will be found that specific gravity numbers confirm the existence of short and long periods, already indicated in the atomic-volume curve of Meyer. The crests of this curve are found to occur first with lithium, sodium and potassium, nearly equidistant (resulting from which we have two short equal periods); but then not again until, after quite a distance, down the catalogue of the elements arranged according to the increasing atomic weights, rubidium is reached. Next, after a similar long distance, the crest occurs with caesium. This important fact of the inequality of the periods is found hidden in the curve of Meyer; as well as the accompanying fact that in the first periods the sinus of the Meyer curve, where $dy/dx = 0$, is at the fourth family of elements, and in the following periods this sinus occurs with the eighth family of elements. In Part I it was shown that the periodicity of the atomic-volume curve was due to the complementary periodicity of the curve of specific gravity; and it was also developed that it is convenient to recognize, as the cause of the periodicity in both cases, the position-numbers of the elements; and that it is more convenient to take these numbers as decreasing from a central maximum in both short and long periods, thus putting them in accord with the observed specific gravities and valencies.

In the present state of our knowledge of physical constants, it is impossible to decide whether any one constant involves such a factor as atomic volume—*i. e.*, whether the complexity of the constant may be simplified by elimination of such a factor as specific gravity, valence or

[1] "Outlines of Inorganic Chemistry," Gooch and Walker.
[2] *Z. anorg. Chem.*, 1904, 41.
[3] *Ibid.*, 1904, 366; *Ber.*, 1905, 1386.
[4] *Ber.*, 1905, 914.
[5] *Chem. News*, 1909, 226.
[6] *J. Chem. Soc.*, 1909, 238.
[7] *Chem. News*, 1909, 148.

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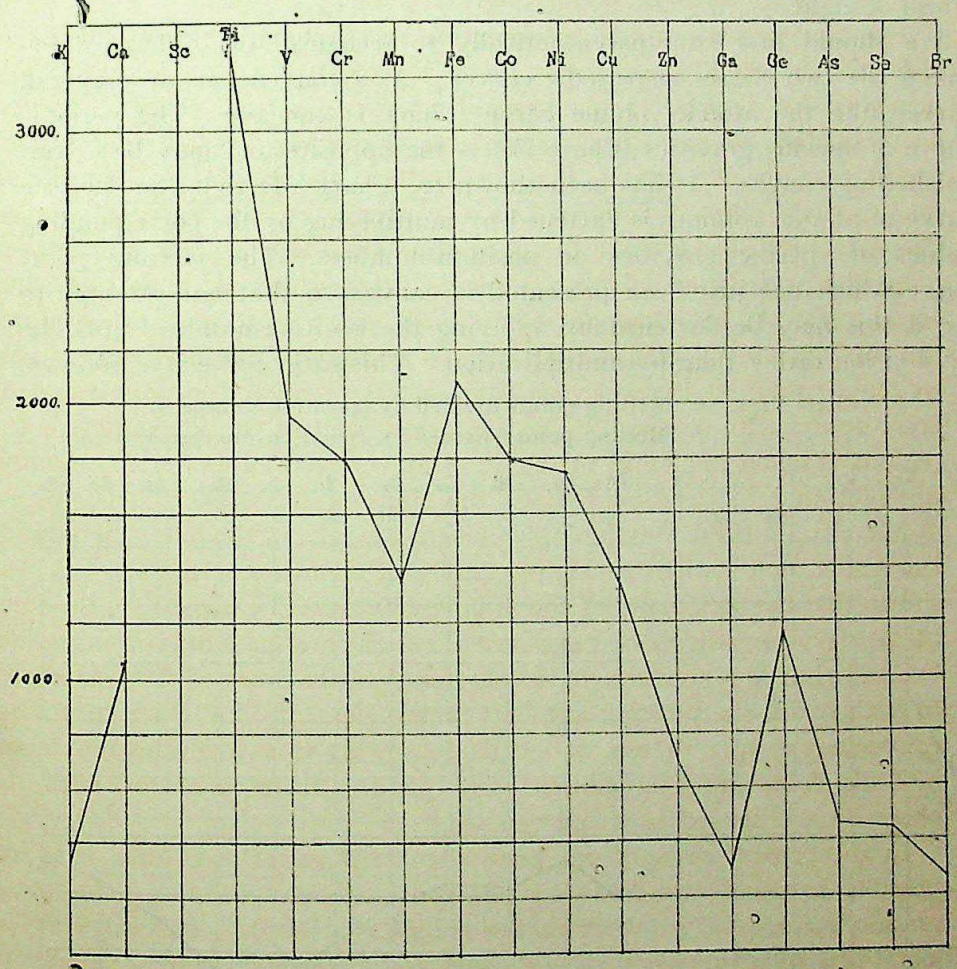
position-number, except by the old test of trial and error. I propose to test in this crude way two constants to see whether their periodic curves are flattened by position-numbers; and by doing this with the long K - - - - Br period to determine whether the positions in that period run to four or to eight.

The melting points of the elements were first arranged to show a periodic curve by Meyer and later by Carnelly. This curve for the first long period (K - - - Br), our basis of illustration, is shown on Chart VII:

Chart VII. Melting points.



It is probable that the temperature of the melting point of any element is fixed by other factors than specific gravity, valence or position-number. Pictet[1] gave a formula involving atomic volume together with the coefficient of expansion of the element. Deer[2] then eliminated

[1] *Compt. rend.*, 1879, 855.
[2] *Chem. News*, 1897, 234.

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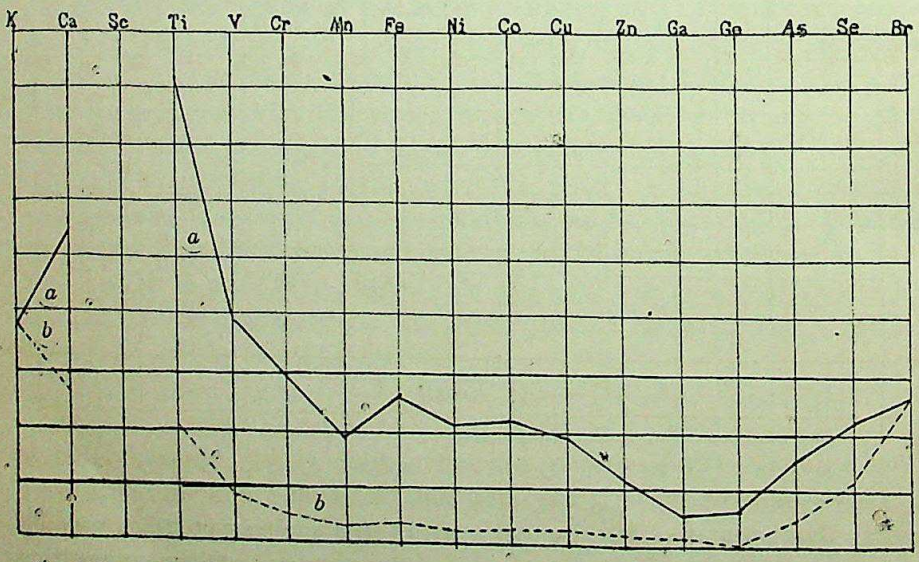
atomic volume from this and obtained portions of a curve which seemed periodic. J. W. Richards[1] introduced the latent heat of fusion, derived from specific heat, into his formula, and Crompton[2] varied the previous formulas by introducing the ratio atomic weight over valence. If, therefore, the curve should be flattened by applying the factor position-number, it would seem as if its periodicity were in part at least determined by the factor which is generally called atomic volume. We may thus get another indication of whether the sequence of numbers used should be those falling from a maximum of four or those falling from a maximum of eight.

We should first stop parenthetically to recognize the difference between the two classes of periodic curves. As a convention, we may call curves like the atomic-volume curve (Chart I) concave. The periodic curve of specific gravities (Chart IV) is the opposite and may be distinguished as convex. It has been shown (*v.* Chart VI) that the concave curve of atomic volumes is flattened by multiplying by the corresponding values of specific gravities or position-numbers. The melting point curve which has just been presented is convex so that our attempt to see if this may be flattened by applying the position-numbers must be by division rather than by multiplication. This ratio curve is as follows:

Chart VIII. *a.* Melting points divided by (position-numbers).
b. Melting points divided by (position-numbers).[2]



The partial flattening of the curve indicates that melting points vary partially at least with the position-numbers; also with the specific gravities—which seems natural. But the important point is that this approx-

[1] *Chem. News*, 1897, 278.
[2] *Z. physik. Chem.*, 1907, 635.

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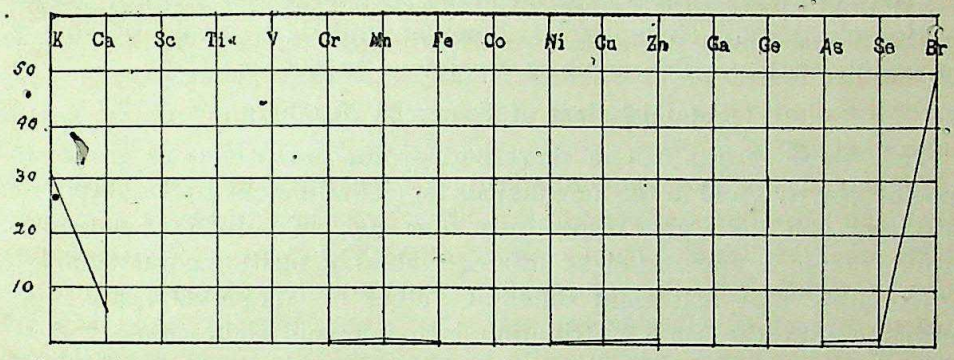
imate flattening could not be obtained if we recognized for this period only position numbers from one to four.

Richards' compressibility figures, already referred to, give for the same period (K...Br) a concave curve which is plotted as follows:

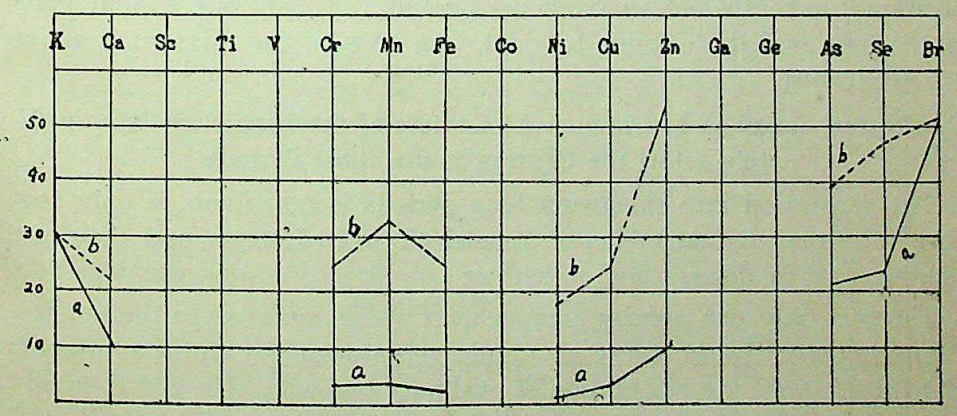
Chart IX. Compressibilities.



This curve is, according to Richards, periodic in the same way that the curve of Meyer is periodic. Let us see if it can be flattened by applying the position-numbers to it. This must be done by multiplying. The result is given as Curve *a* in the following chart:

Chart X.

a. Compressibilities x (position-number); *b*. Compress's x (position-number).^{2}



The value $y =$ *constant* is evidently more closely approximated in this curve than in the original one; and this would indicate, if it were perfect, that compressibilities vary with specific volumes. This would seem natural also and is the reverse of the finding for melting points. I have found that a better result is obtained by multiplying by the square of the position-numbers as shown by curve *b* in Chart X above. The values plotted are closer to a constant value in this case and indicate that compressibilities vary approximately with the squares of specific

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volumes or inversely as the squares of specific gravities. Fessenden[1] published a formula for rigidity in which this property is shown to vary inversely as (atomic volumes)$^{5/3}$, but when temperature is taken into consideratio nrigidity varies inversely as (atomic volumes)^2, which is effectively the factor used in curve *b* above. From this work he derives figures in good accord with those experimentally determined for Young's modulus for elasticity. These results, however imperfect, would be simply impossible with position-numbers from four to one.[2]

Establishment of Sequence Numbers.

Since these results call in short periods for four different grades of specific gravities and in the long periods for eight different grades of specific gravities, and these give respectively four and eight different values of atomic volumes, four and eight different values of melting points and approximately four and eight different values of compressibilities, it is probable that the same distribution into four and eight values will be found for many other physical properties which may be said to depend upon the fundamental physical property, specific gravity; and since this is seen to be connected with the orderly sequence of the elements according to their atomic weights, the position-number which indicates this chemical relation (and which binds together all the above physical properties) has been chosen in the previous section as the fundamental chemical property; and in this connection it is emphatically evident that the position-numbers which in the short periods run from one to four must in the long periods continue to eight, else none of the facts cited above are explicable.

Conformity Attained by Placing the Centers of the Long Periods Immediately below the Centers of the Short Periods.

The separation into short and long periods is not given, is only suggested, by the original tables of Mendeléeff and of Meyer and there are relationships in these tables which are not in accord with this idea.[3]

There is only one concise arrangement which conforms to the requirements imposed by the curve of atomic volumes and by all the arguments which lead up to the recognition of position-numbers. The eighth family of the long periods must be placed immediately below the middle ele-

[1] *Chem. News*, 1892, 206, 217.

[2] The effect of (sequence numbers)^2 on the melting points is shown by curve VIII (*b*) above.

[3] The eighth family has always been beyond the system. Attempts to establish a "valence of eight" for members of this family have failed to impress students of this subject. Also, the discovery of the non-valent family, falling as it does in the periods of the Mendeléeff table in alternation with the eighth family, failed to give the expected assistance, since there is no similarity between these families.

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ments of the short periods—the eighth family below carbon and silicon.[1] The elements of highest specific gravity are thus placed on a common axis and the other elements range out from this axis symmetrically on either side according to their gradually decreasing specific gravities.

Arrangement in Accord with Position-Numbers and Specific Gravities.

The table proposed is arranged according to the requirements enumerated above. Thomsen in 1895[2] published a table founded upon purely arithmetical grounds, similar to this but more extended in the lower portion. This was approved by Richards[3] but modified for simplicity in this same lower portion, so that Richards' table is in all essentials identical with the one now proposed. For the arrangement of the elements of the rare earths in the lower portion of the table, I am indebted to a printed wall-chart of the elements published by Baskerville. The figures at the heads of the columns indicate not only position numbers but also approximate specific gravities. They indicate also in certain cases the valence towards hydrogen and in other cases (by subtracting these figures from eight) in general the upper valences towards oxygen, as shown in the succeeding paragraph.

CHART XI.—THE PERIODIC SYSTEM.

1	2	3	4	5	6	7		8		7	6	5	4	3	2	1	0
					1	2	3	4	3	2	1	0					
					Li	Be	B	C	N	O	F	Ne					
					Na	Mg	Al	Si	P	S	Cl	A					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Yt	Zr	Nb	Mo	...	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	Nd	Pr	...	Sm	Eu	Gd	Tb	...	Er	...	Tu	Yb	...	...
...	...	...	...	Ta	W	...	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	...	...	...
...	Ra	...	Th	...	U	...	...	...	...	...	...	...	...	...	...	...	...

Valence Relations.

Without attempting to open the question "What is valence?" it would seem from the discussion in the previous portion that there is evident, especially in the short periods, some relation, as yet unknown, between the simplest valences and specific gravities. In the long periods, this relation of valence towards hydrogen is obscure; but then the relations

[1] This does not exclude but rather confirms the possibility of an arrangement whereby at one end of the series potassium and sodium are symmetrically opposed to each other and at the other end bromine and chlorine are so placed—as developed in much detail and with great wealth of illustration in the February number of the *American Chemical Journal* by my colleague, Professor B. K. Emerson.

[2] *Loc. cit.*

[3] *Chem. News*, 1898, 194.

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of the oxygen valences become of interest. On the right, in the K...Br period, we have the non-metals in their sequence (Br—Se—As—etc.), the upper valences of which may be 7—6—5—etc., gradually decreasing as the specific gravity rises. On the left, we have the metals (K—Ca—Sc—etc.), the highest valences of which are gradually increasing as the specific gravity increases. This latter tendency may be followed to chromium with a valence of six and manganese with valence seven, so that the next logical step would give to the eighth family a valence of eight, were it not that at this point there is met the tendency from the right towards a valence of zero. The arrows on the chart are intended to indicate these opposing tendencies. From the one side the tendency is to give the iron family a valence of eight and from the other to give a valence of zero so that the resultant might be any valence. Therefore, although it is inexplicable that the elements of this family tend toward a valence of two and three, yet with the two tendencies meeting here, some abnormal valence is to be expected. Again, it is normal that copper, silver and gold should be reckoned univalent; and zinc, cadmium and mercury bivalent; if we take into account the tendency towards decreasing oxygen-valence which began with bromine. This is just as normal as that chromium and manganese should have possible valences of six and seven and that the iron family should have a valence of neither eight nor zero. The univalence of copper and silver is seen to be due to a reason just the opposite of that for the univalence of potassium. Copper is thus seen to mask as a very poor metal ("noble," inert) because it is the last, heaviest of the non-metals in the period. Potassium is a true metal, of low specific gravity, base-forming, active. It is evidently an error to place these two metals in one family as they appear on the Mendeléeff chart.

The Length of the Last Periods.

Beyond the two long periods and beginning with caesium, any arrangement of the elements, in the present state of our knowledge, must surely be tentative. I have chosen the arrangement given because it allows, as Baskerville states, a place for each element that is accurately known; also because it is concise. The length of these last periods has never been indicated by any data. It is my belief that light will be thrown most promptly upon the question of the arrangement of the lower periods by increasing our knowledge of the specific gravities of the pure elements. We can then finish plotting the charts of the periodic curves of specific gravity and position-number (*v.* Part I, Charts IV and VI). It may be that these periods should be much longer, *i. e.*, that the position-numbers should run from one to possibly sixteen; or that the eighth family should in these periods contain (*e. g.*) six rather than three members; or that we should have here a return to short periods of eight members. But this

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question must wait further knowledge either of the number or of the physical properties—especially the specific gravities—of the rare-earth elements.

Summary.

It has been shown in Part I that, in physical calculations, symmetry is often more surely obtained by neglecting atomic weights and substituting specific gravity, valence or position-number in the place of atomic weight; that a harmonic relation, which has not been previously sufficiently recognized, exists between these three properties in any one period. In Part II there has been proposed an arrangement of the periodic system, slightly different from the usual one but in harmony with the fundamental physical property specific gravity, and more rational especially in regard to the heavy metals of the long series.

AMHERST COLLEGE,
AMHERST, MASSACHUSETTS.

THE DIFFUSION OF OXYGEN IN WATER.

BY TOR CARLSON.

Received April 1, 1911.

In a previous investigation[1] it was shown from determinations of the rate of solution of carbon dioxide and oxygen in water or the rate of escape of the gases from water that, if one adopts Nernst's theory for the phenomenon of solution, the ratio between the coefficients of diffusion of the gases mentioned may be calculated to be 1.158. For the coefficient of diffusion of carbon dioxide there are available closely concordant values obtained at 16° by two different observers, *viz.*: 1.36 and 1.41 (per sq. cm. per 24 hours) by Stefan,[2] and 1.37 by Hüfner,[3] who used hydrophane plates. For oxygen, moreover, Hüfner (with hydrophane plates and counter-diffusion of nitrogen) found 1.62 at 16°, and Hagenbach,[4] in water containing 20 per cent. gelatin, obtained the value 7.58 at 14°; but in each case only one determination was made. Hagenbach also states that the gelatin offered greater resistance to the diffusing gas molecules than pure water, which in a 20 per cent. gelatin solution was on an average 1.5 times as great. Consequently the coefficient of diffusion for oxygen in water in Hagenbach's experiment amounts to 11.37 (14°) per square centimeter per 24 hours.[5] If the coefficient of carbon dioxide be taken as 1.38 (16°), the mean of the above three determinations, then the ratio between the coefficients of diffusion for oxygen and carbon dioxide

[1] Tor Carlson, *Meddel. fran Vet. Akad. Nobelinstitut.*, Vol. II, No. 5, 1911.

[2] *Sitzb. Wien Akad.*, 77, Abth. II, 37 (1878).

[3] *Wied. Ann.*, 60, 134 (1897).

[4] *Ibid.*, 65, 673 (1898).

[5] For the carbon dioxide in a 20 per cent. solution of gelatin Hagenbach obtained the numbers 0.843 and 0.770, giving the mean value 1.21, calculated as above for water.

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according to Hüfner's experiments would be 1.174, and according to Hagenbach's 8.839 (uncorrected), or in the latter case about 7 times as great as in the former.

It is therefore of special interest to obtain a new determination of the diffusion coefficient of oxygen. As is well known, Wroblewsky[1] was the first to attempt to ascertain the law in accordance with which carbon dioxide diffuses in water. His attempt failed because, when he allowed the gas to enter at the top of a column of water, the upper layers were first saturated with it, and hence became heavier and sank, thus causing currents in the water which disturbed the steady process of diffusion. Soon afterwards,[2] however, Stefan proved that the occurrence of currents (and their disturbing influence) depends on the width of the test-pipe, and that they might be almost entirely prevented if the cross section of the pipe were made small enough, at most 1 millimeter. With such pipes Stefan succeeded in proving the correctness of the assumed law regarding the diffusion of carbon dioxide in water and alcohol, *i. e.*, he proved that Fick's supposition in accordance with which the movements of a salt through its solvent follow analogous rules to those demanded by Fourier's theory of the conduction of heat, is also applicable to the diffusion of dissolved gases in fluids. Stefan's experiments were of two kinds, in one kind, the carbonic acid was made to traverse a column of fluid made as long as possible, and assumed to be infinitly long, while in the other the gas had access to the open air through a short column of water. It is evident, however, that when experimenting with a gas whose coefficient of absorption is relatively small, like that of oxygen in water, Stefan's method is not very suitable. In order to obtain an accurately measurable diminution of the volume of gas in such a case, too long a time would be necessary for the experiment, and even supposing it were possible to keep the temperature constant, considerable disturbances would be inevitable, owing to the evaporation of the fluid.

Agar-agar or gelatin solution may be used for determinations of diffusion (compare Pringsheim,[3] Hoppe-Seyler,[4] and Voigtländer,[5] etc., on diffusion of saline solutions), and by this means currents due to variations of density may be avoided, as was proved by Hagenbach's experiments with gases which are indifferent to gelatin. As regards oxygen, however, the high value of the diffusion coefficient arrived at by Hagenbach[2] is in all probability to be attributed to a process of oxidation in the gelatin, so that the figures given by him represent not only the amount of oxygen which diffused, but also the quantity which was chemically absorbed.

[1] *Wied. Anns*, 2, 481 (1877).
[2] *Loc. cit.*
[3] *Z. physik. Chem.*, 17, 473 (1893).
[4] *Ibid.*, 59, 411 (1894).
[5] *Ibid.*, 3, 313 (1889).

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At the suggestion of Professor Svante Arrhenius I added potassium chloride (about 1 per cent.) to the diffusion liquid. The reduction in the diffusion of the oxygen caused by this is relatively slight, as proven by Arrhenius'[1] investigations of the rate of diffusion of acetic acid in water and in normal potassium chloride solution (decrease 0.3 per cent.) and by Abegg's[2] on that of ammonia in water and in about normal potassium chloride solution (decrease 0.8 per cent.).

The diffusion experiments which I shall describe were carried out in the following manner. To each of two plane parallel plate-glass slabs, pressed against each other by springs, half a glass tube of even caliber (about 4.5 cm. in diameter) was carefully cemented. The tube fixed in the lower slab was narrowed at the free end, and continued by a three-way cock. The upper tube was finished off by a plane slab of glass in the center of which a capillary tube was inserted. By means of a screw contrivance of small pitch the upper slab could be cautiously pushed along the lower, so that the two glass tubes were made to occupy different positions in relation to one another; and in each slab there was inserted a three-way glass cock. The lower cylinder was filled with as much mercury as was required to make the height of the diffusion fluid the same in both halves of the cylinder.

The quantity of gas passing through a cross section of the cylinder in an infinitesimally short time is proportional to the concentration at the cross section, to this infinitesimal time interval, and to the rate of alteration of the concentration of the gas, at the cross section considered. If the concentration of the gas be represented by r, then $-dr/dx$ is the alteration of the concentration in any section, the position of which is determined by the distance x, measured along the length of the cylinder. The quantity passing through a section q in a certain interval of time is therefore expressed by

$$m = -k.\ q.\ dr/dx.\ dt,$$

where k represents the coefficient of diffusion. Since r is a mass divided by a volume, it will easily be seen from this formula that k signifies a surface divided by a time. If the difference of the quantity of gas which during the time dt passes through the end surface of a small length dx of the cylinder be expressed by $(m + dm/dx.\ dx) - m$, and this be divided by the increase in quantity, which takes place in this small length during the same period we have

$$-dm/dx.\ dx = q.\ dx\ dr/dt.\ dt,$$

whence for r we obtain the differential equation,

$$dr/dt = k.\ d^2r/dx^2.$$

[1] *Z. physik. Chem.*, 10, 51 (1892).
[2] *Ibid.*, 11, 248 (1893).

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The solution of this equation, in cases where it treats of a limited column of fluid, gives r in the form of a periodical series, and from that, by a well known method, one may calculate the amount of gas escaping from the lower half of the tube. Again, if at the time $t = 0$ the distribution of the gas in the liquid is such that one part of the cylinder shows the constant concentration a, while another part has the concentration O, then the mass of gas A, passing through the surface of separation between these two parts, during the time t, is given by the expression[1]

$$A = a.q\sqrt{k.t/\pi}.$$

This formula, strictly speaking, is only applicable in those cases where the two parts of the cylinder are infinitly long, but it may be used for cylinders of finite length, if the time of experiment be so chosen that variations in the condition of the two end strata during this time may be disregarded in comparison with the accuracy attained in the measurement. According to Stefan[2] this formula can invariably be employed for movements of diffusion, provided that the quantity $\pi^2 . k . t > l^2$.

In the experiments in question, $k < 2$, $t < 9$ and $l = 11.2$, so that the limiting value was not reached even in the most unfavorable case.

The diffusion experiments were carried on in the following manner: the upper cylinder, placed immediately above the cock in the lower slab, was filled with air-free distilled water which was allowed to run through it from the bottom upwards for 15 to 20 minutes, afterwards the cock was closed and the capillary tube shut off by a rubber band with a glass stopper inserted into it. At the same time a 1 per cent. potassium chloride solution, in which oxygen, or in other cases carbonic acid gas, had previously been dissolved, was made to run through the lower cylinder by means of a glass tube which opened on the surface of the mercury. When the cylinders had been filled in this manner, the front part of the upper glass slab was pushed above the free portion of the lower cylinder, the whole apparatus being set up (with the cylinders in an exactly vertical position) on a firm base, free from possibility of vibration, in a basement room with double walls of masonry. The variations of temperature in the room during the time the experiments were carried on amounted to only $\pm 0.2°$ (measured by a self-registering Richards thermometer). When the contents of the cylinders had come to the temperature of the room, the upper cylinder was screwed on to the lower, and the precise time noted.

After a certain number of days the cylinders were pushed past each other till the cock in the upper slab stood exactly above the lower cylinder. In order to prevent the fluid coming in contact with the air, the contents of the cylinders were taken out for analysis by forcing mercury from a

[1] Stefan, *Sitzb. Wien Akad.*, 79, Abth. II, 177 (1879).
[2] *Loc. cit.*

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level-tube into the lower cylinder, where it displaced the diffusion fluid, which then passed to a tube, filled with mercury, of the same capacity as the cylinders, the tube at either end being provided with a three-way Miescher-Geissler cock. During this displacement the mercury ran out of the tube at the same rate as the fluid was forced in. Subsequently the upper cylinder was placed above the surface of the mercury, which was now on a level with the upper surface of the lower slab, and its contents forced out in the same manner.

The quantity of oxygen dissolved was determined by Winkler's[1] method: Through the one-cock of the analysis tube 3 cc. of an alkaline potassium iodide solution were introduced, and through the other 3 cc. of a solution of manganese chloride while a corresponding quantity of fluid was allowed to run off. The precipitate was dissolved by means of 5 cc. of concentrated hydrochloric acid forced under it; the solution was washed into a beaker, and titrated with 0.01 N thiosulfate and starch.

In the experiments with carbon dioxide, the diffusion fluid was collected in a beaker filled with air free from carbon dioxide, and containing a solution of barium hydroxide and barium chloride. After the solutions had stood for 24 hours, the excess of barium hydroxide was titrated with $^1/_{20}$ N hydrochloric acid and phenolphthalein.

The water, boiled in vacuum and run through the upper cylinder, may be considered (excluding experimental errors) to be free from air; by Winkler's method the presence of 0.01–0.02 cc. oxygen per liter of water could be detected.

The following experiments were made at an average temperature of 18.2° (± 0.2). The length (l) of each diffusion cylinder was 11.2 centimeters. In the table t represents the time of diffusion expressed in days; a_I, quantity of diffused oxygen (carbon dioxide respectively) in cubic centimeters per liter, in the diffusion fluid from the upper cylinder when the experiment was interrupted; a_{II}, the corresponding quantity in the fluid of the lower cylinder; k, the constant of diffusion per square cm. per day.

Therefore $a_I = a_I + a_{II}/l \cdot \sqrt{k.t/\pi}$.

Carbon Dioxide:

	I.	II.	III.	Mean.
t	7	5	9	...
a_I	94.4	92.8	123.7	....
a_{II}	489.4	583.2	532.4	...
k	1.472	1.487	1.466	1.475

Oxygen:

	I.	II.	III.	Mean.
t	6	6	5.9	...
a_I	3.95	15.24	18.28	...
a_{II}	20.58	2.96	3.48	...
k	1.702	1.745	1.713	1.720

[1] *Ber.*, 22, 1764 (1889).

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If the above coefficients of diffusion be corrected to 16° (corr. 3 per cent. per degree), we get $k_{CO_2} = 1.378$ and $k_{O_2} = 1.607$, and it is evident that they agree fairly well with the values of Stefan and Hüfner (cited above). Hagenbach's figures (11.37 uncorr.) for the diffusion of oxygen in water must therefore be considered quite incorrect, due to the source of error mentioned above. Further, the ratio between the coefficients of oxygen and carbon dioxide, according to the above experiments, is *1.166*, and this result closely approximates to that calculated for the gases in question from the measurement of the rates of escape of the gases from solution.[1]

Finally, the relation of the results may be considered to be the so-called Exner Rule, according to which the rate of diffusion of a gas is inversely proportional to the square root of its density.

That is, $k_{O_2} : k_{CO_2} = \sqrt{1.5202} : \sqrt{1.1056} = 1.173$.

This result closely agrees with the ratio obtained in the above research.

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THE FORMATION OF DOUBLE SALTS.

[FOURTH PAPER.]

BY H. W. FOOTE AND P. T. WALDEN.

Received May 1, 1911.

In two previous articles from this laboratory[2] the double salts which form from water have been compared with those which form from non aqueous solvents at the same temperature. It was shown that when a double salt crystallizes from water with water of crystallization, the latter in general appears to be an essential constituent of the salt, and the substitution of another solvent may affect the type of double salt produced giving an entirely different ratio between the single salts and between these and the solvent of crystallization. On the other hand, double salts which crystallize from various solvents without combining with them appear always to form the same types. In short, double salts with solvent of crystallization are really triple molecular compounds and have no necessary type relation to the true double salt, which is essentially a dual molecular compound.

It is evident that a double salt may form without solvent of crystallization from certain solvents, giving always the same types, and may combine with others, changing the type of salt. In the present investigation, mixtures of cupric chloride with potassium chloride and with ammonium chloride have been studied. Both systems have been thoroughly investigated previously in water solution and only hydrated double salts ob-

[1] Tor Carlson, *Meddel. fran Vet. Akad. Nobelinstitut.*, Vol. II, No. 5, 1911.
[2] THIS JOURNAL, 32, 618 (1910); 33, 459 (1911).

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tained at 25°. Using alcohol as solvent in one case and both alcohol and acetone in the other, we have obtained double salts which did not combine with the solvents and they were different in type from the hydrates.

I. Potassium and Cupric Chlorides.

The double salts which form from water have been very thoroughly investigated by Meyerhoffer.[1] He found that up to 57° only one double salt, $2KCl.CuCl_2.2H_2O$, is produced from water while above this temperature the anhydrous 1 : 1 salt can be obtained. Meyerhoffer also noted that the anhydrous salt can be obtained by crystallization from acetic acid containing a little water. We have determined the solubility relations at 25° of potassium and cupric chloride in varying proportions in both absolute alcohol and acetone and in each have obtained the 1 : 1 double salt without solvent of crystallization.

The anhydrous cupric chloride used in this work was prepared by heating the recrystallized dihydrate at 130–140° to constant weight. The method was entirely satisfactory. Absolute alcohol and acetone were obtained by redistilling the best commercial products. In the case of alcohol, sodium was added before distilling and only the middle distillate was used.

In the first experiments, salts and alcohol were mixed in varying proportions and shaken in glass-stoppered bottles in the thermostat at 25°, usually for two days or more. The method was the same which has been used repeatedly for double salt work, but in this case we were unable to obtain consistent results. It became evident after considerable work had been done that complete equilibrium was not being reached. This appeared to be due partly to the fact that the potassium chloride was quite insoluble in the alcohol, which made reaction very slow, and partly to there being small lumps present which were not thoroughly disintegrated even by long shaking and repeated crushing in the bottle. The difficulty was entirely overcome by placing in the bottles a number of short glass rods. The rods were long enough to prevent their becoming wedged crosswise in the bottles but also short enough to allow considerable play so that when the bottles were rotated, the rods kept falling, first at one end of the bottle and then at the other. We think that this device is more serviceable than placing glass or metal beads in the bottle, as the rods have more weight and strike a harder blow. Certainly the arrangement made the difference between success and failure in our own work for we had no further difficulty in reaching equilibrium. We believe the device will be of service whenever equilibrium is to be reached by reaction between difficultly soluble solids in contact with solutions.

[1] *Z. physik. Chem.*, 3, 336 (1889); 5, 97 (1890).

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In analyzing the solutions, copper was usually determined by titrating with sodium thiosulfate after addition of potassium iodide, using starch solution to determine the end point. The amount of potassium chloride in solution was very small and was usually not determined. When necessary to determine it, however, copper was removed by hydrogen sulfide and potassium weighed as chloride. The residues were heated at 130°–140° to determine alcohol or acetone and copper determined by thiosulfate. Potassium chloride was calculated by difference. The residues were exceedingly fine and usually retained a small amount of solvent mechanically. When this was small in amount, and evidently not an essential part of the residue, the results are usually calculated free from solvent, as will be seen.

The following results were obtained, using alcohol:

TABLE I.—SOLUBILITY OF POTASSIUM-CUPRIC CHLORIDES IN ABSOLUTE ALCOHOL AT 25°.

No.	Per cent. $CuCl_2$ in solution.	Per cent. KCl in solution.	Per cent. $CuCl_2$ in residue.	Per cent. KCl in residue.	Per cent. alcohol in residue.	Residue contains
1	1.27	(0.28)[1]	15.88	84.12	...	KCl and
2	1.51	(0.28)[1]	57.43	42.57	...	$KCl.CuCl_2$
3	2.15	...	64.04	35.60	0.36	
4	5.25	...	64.24	35.46	0.30	$KCl.CuCl_2$
5	30.16	...	65.34	32.02	2.64	
Calculated for $KCl.CuCl_2$			64.32	35.68	...	
6	34.17	(0.21)[1]	67.91	21.35	10.74	$KCl.CuCl_2$
7	34.45	(0.21)[1]	70.88	12.38	16.74	and
8	34.29	(0.21)[1]	72.48	7.29	20.23	$CuCl_2.C_2H_5OH$
9	33.97	0.00	75.83	0.00	24.17	$CuCl_2.C_2H_5OH$
Cal. for $CuCl_2.C_2H_5OH$			74.48	...	25.52	

The results in the table show clearly that one salt only forms at 25° from alcohol. The salt was present in pure condition in numbers 3–5 where the composition of the solution varies widely and the residue is practically constant. In numbers 1–2, with constant solubility and variable residue, potassium chloride and double salt were the solid phases. Number 9 shows the solubility of pure cupric chloride at 25°, and also the composition of the solid phase which evidently contains one molecule of alcohol.

The results using acetone as solvent are given in Table II. Equilibrium was obtained without any difficulty using glass rods in the bottle as described before, but on the other hand, a new and quite unexpected complication presented itself. In the first experiments, the bottles were rotated at 25° for several days and after a time the solution darkened and decomposition set in. The reaction was not specially investigated,

[1] The average of two determinations made in preliminary work. Potassium was not directly determined in the series given above.

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but there appears to be a slow action of the cupric chloride on the acetone, producing cuprous chloride which is at first held in solution but may afterwards precipitate, affecting the composition of both solution and residue. The action appears to be negligible for the first twenty-four hours but when once begun seems to run more rapidly. The series of results given below was obtained by rotating the bottles for not more than twenty-four hours. The residues in numbers 1–5 were dried at 130°–140° before analysis to free them from traces of included acetone.

TABLE II.—SOLUBILITY OF POTASSIUM-CUPRIC CHLORIDES IN ACETONE AT 25°.

No.	Per cent. $CuCl_2$ in solution.	Per cent. KCl in solution.	Per cent. $CuCl_2$ in residue.	Per cent. KCl in residue.	Per cent. acetone in residue.	Residue contains
1	0.34	(0.38)[1]	6.31	93.69	...	KCl and
2	0.34	(0.38)[1]	59.94	40.06	...	$KCl.CuCl_2$
3	0.48	...	64.39	35.61	...	
4	1.50	...	64.23	35.77	...	$KCl.CuCl_2$
5	2.06	...	65.00	35.00	...	
Calculated for $KCl.CuCl_2$			64.32			
6	2.49	0.27	65.13	32.75	2.12	$KCl.CuCl_2$ and
7	2.32	...	75.24	11.79	12.97	$CuCl_2.C_3H_6O$

The results show the formation of the same anhydrous 1 : 1 salt that was obtained from alcohol. This was to be expected provided the acetone did not enter into the compound. The solubility relations are entirely different from the first case, due to the much smaller solubility of cupric chloride in acetone.

The composition of the limiting solutions between which pure double salt forms is shown by numbers 1–2 and 6–7. The pure double salt was present in numbers 3–5. The acetone found in the residues, numbers 6–7, is only approximately correct as acetone is lost very rapidly indeed by the cupric chloride while being freed from the mother liquor and water is taken up. For the same reason it was difficult to determine the composition of the pure cupric chloride acetonate. The solubility of pure cupric chloride in acetone was found to be 2.49 and 2.32 per cent. in two experiments, but one of the residues gave, on drying, an amount of acetone several per cent. below the calculated value for $CuCl_2.C_3H_6O$, and another, not so thoroughly dried, several per cent. more than the theoretical. There can be no doubt, however, that the above formula for the acetonate is correct, corresponding to the alcoholate.

II. Ammonium and Cupric Chlorides.

A number of hydrated double salts of ammonium and cupric chlorides have been described but the investigation of Meerburg[2] has shown quite conclusively that the compound $2NH_4Cl.CuCl_2.2H_2O$ is the only stable

[1] Determined in preliminary work.

[2] *Z. anorg. Chem.*, 45, 1 (1905).

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double salt that forms from water between —11° and 80°. No anhydrous salt has been described, though Meyerhoffer[1] mentions briefly that he obtained one.

In our work mixtures of the single salts were treated with alcohol just as in the previous case. Glass rods were used in the bottles to assist in reaching equilibrium. In analyzing solutions, only copper was determined (by titration with thiosulfate as before) as the amount of ammonium chloride dissolved was very small, and the solubility relations are sufficiently clear from the data found for cupric chloride alone. The residues were very fine and always included a small amount of alcohol. In the table, the composition of the dry residue is given except in the last two results, where the alcohol formed a compound.

The following results were obtained:

TABLE III.—SOLUBILITY OF AMMONIUM-CUPRIC CHLORIDES IN ABSOLUTE ALCOHOL AT 25°.

No.	Per cent. $CuCl_2$ in solution.	Per cent. $CuCl_2$ in residue.	Per cent. NH_4Cl in residue.	Per cent. alcohol in residue.	Residue contains
1	4.65	10.70	89.30	...	NH_4Cl and $NH_4Cl.CuCl_2$
2	4.74	63.54	36.46	...	
3	6.45	71.45	28.55	...	$NH_4Cl.CuCl_2$
4	12.90	72.33	27.67	...	
Cal. for $NH_4Cl.CuCl_2$		71.53	28.47	...	
5	34.92	72.54	24.56	2.90	$NH_4Cl.CuCl_2$ and $CuCl_2.C_2H_5OH$
6	34.50	74.04	8.09	17.87	

The single 1 : 1 salt is the only one formed. It is entirely different in type from the hydrated double salt but corresponds to the potassium cupric compound, which it also resembles in color.

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EQUILIBRIUM IN THE SYSTEM: LEAD NITRATE AND PYRIDINE.

BY JAMES H. WALTON, JR., AND ROY C. JUDD.

Received May 3, 1911.

Pyridine occupies in many ways a unique position among organic solvents. Not only does it dissolve many organic compounds—such as the fats, oils and certain of the carbohydrates—but it also exercises a solvent action on a large variety of inorganic compounds. Moreover, just as water unites with many of these inorganic compounds as water of crystallization, so many of them take up pyridine of crystallization. With pyridine, types of solubility curves have been obtained which are analogous in every way to those resulting from solubility determinations when water was used as a solvent.

[1] *Z. phys. Chem.*, 3, 340 (1889).

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Tombeck[1] has made certain solubility determinations with pyridine, but by far the greater part of the work on this subject has been carried out by Kahlenberg[2] and his students, who have investigated the solubility in pyridine of the nitrate, chloride, bromide and iodide of silver, and also of mercuric chloride. The following research forms a part of an extensive investigation which is still being carried on in this laboratory.

It has been known for some time that lead nitrate is soluble in pyridine. In 1897 Schmujlow[3] described the compound $Pb(NO_3)_2.3C_5H_5N$. In 1898 Pincussohn[4] working with precipitates thrown down by the addition of water to solutions of lead nitrate in pyridine made and described $Pb(NO_3)_2.2C_5H_5N$ and $Pb(NO_3)_2.C_5H_5N.HNO_3$. The object of this investigation was to establish the solubility curve of lead nitrate in pyridine and to ascertain what compounds are in equilibrium with the saturated pyridine-lead nitrate solution at the various temperatures.

Materials Used.—The lead nitrate, which was obtained from Merck, was recrystallized and thoroughly dried. The pyridine was also obtained from Merck. It was first dried over fused potassium hydroxide, then boiled with potassium permanganate and distilled off. The distillate was then boiled with barium oxide for five hours,[5] using a reflux condenser. This distillate was then redistilled from fresh barium oxide, the portion coming over between 114° and 115° being used in the investigation. This purified pyridine was kept in glass-stoppered bottles which were capped with thin sheet rubber.

The thermometers used were graduated to one-tenth of a degree, and the temperature could easily be estimated to one one-hundredth of a degree. They were standardized by comparing them with an instrument which had been checked by the Bureau of Standards. Below 0° a toluene thermometer was used.

Methods of Analysis.

Gravimetric.—For the estimation of the lead in the pyridine solution, two methods were available: gravimetric, weighing the lead as lead sulfate, and volumetric by means of the well-known ammonium molybdate titration.

The gravimetric method was first employed and was carried out as follows: The solution of lead nitrate in pyridine was placed in a casserole, about 50 cc. of water were added, then 5 cc. of concentrated nitric acid (sp. gr. 1.42). The solution was then boiled, and after cooling 3 cc. of sul-

[1] *Ann. chim. phys.*, [7] 21, 433 (1900).
[2] *J. Physic. Chem.*, 12, 283 (1908); *Ibid.*, 13, 421 (1909); *Ibid.*, 14, 189 (1910).
[3] *Z. anorg. Chem.*, 12, 1 (1897).
[4] *Ibid.*, 14, 379 (1898).
[5] Wilcox: *J. Phys. Chem.*, 14, 576 (1910).

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furic acid (sp. gr. 1.84) were added to convert the lead to the sulfate. The pyridine and nitric acid were now expelled by evaporating to the fumes of sulfuric acid, water and alcohol were then added to the cold solution and the lead sulfate filtered on a Gooch crucible, then washed, dried and weighed in the usual manner.

The gravimetric method was unsatisfactory for two reasons: in the first place, the lead when precipitated from the solution containing pyridine came down as a dark colored slimy precipitate which was difficult to filter, and which crept up on the side of the casserole so badly that mechanical loss was almost inevitable. In the second place the gravimetric method was too slow. It was necessary to stir the lead nitrate-pyridine mixture until a state of equilibrium had been reached. This could be ascertained by taking and analyzing samples of the solution from time to time. Upon analyzing two consecutive samples and obtaining the same results it could safely be assumed that the solution was saturated with respect to the lead nitrate. Obviously such a method for analyzing the pyridine solution required a method of analysis which was not only accurate but rapid as well, and the gravimetric method did not fulfil the second requirement.

The Volumetric Method.—A solution of ammonium molybdate was prepared and standardized by weighing out samples of pure lead nitrate, converting them to the sulfate by heating with concentrated sulfuric acid, dissolving the sulfate in ammonium acetate and titrating in the usual way using tannic acid as an indicator. One cubic centimeter of this solution was equivalent to 0.01300 gram of lead nitrate.

Before the volumetric method could be used it was necessary to see whether or not a solution of ammonium acetate containing lead nitrate and some pyridine gave the same value when titrated with molybdate solution as an ammonium acetate solution containing lead sulfate instead of the nitrate, and no pyridine.

To test this point samples of pure lead nitrate were dissolved in ammonium acetate solutions, pyridine added, and the titration carried out by means of ammonium molybdate as in the standardization with lead sulfate. The following table shows the results of these experiments:

Experiment.	Wt. of $Pb(NO_3)_2$ taken.	Wt. of $Pb(NO_3)_2$ found.	Volume of the solution.
1	0.2196	0.2197	100 cc.
2	0.2196	0.2194	100 cc.
3	0.2196	0.2196	100 cc.

In each of these determinations 3 cc. of pyridine were added to the solution, which was then boiled until the odor of pyridine could no longer be observed.

The above experiments show that the lead may be titrated when pres-

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ent in the solution as lead nitrate and moreover that the presence of a small amount of pyridine does not influence this determination.

In the subsequent volumetric determination of lead the method just described was closely followed.

The Meyerhoffer and Sanders apparatus was used in making the solubility determinations. The particular form consisted of a hard glass test tube ten inches long and two inches in diameter immersed in a constant temperature bath. The tube was fitted with a stirrer which turned in a mercury seal (Fig. 1), thus preventing the loss of solvent by evaporation or the admission of moisture from the air. To take a sample the weighing tube A was introduced into the larger tube through a hole in the stopper. After coming to the temperature of the bath the stirrer was stopped, the end of the small tube B, which was covered with a piece of closely-woven muslin, was dipped below the surface of the pyridine and filled by applying suction at C. A was then removed, stoppered, weighed and the contents analyzed.

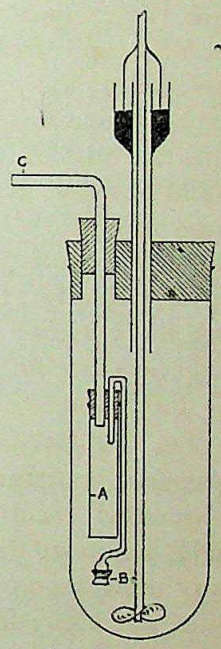

Fig. 1.

In working at 0° the thermostat was filled with finely crushed ice and water. Below that temperature freezing mixtures were used. From 0° to 50° water alone was used, the temperature of the bath below 25° being kept lower than that of the room by means of a spiral tube through which water at the temperature of 5° was allowed to flow. From 50° to 90° the water in the bath was covered with a layer of paraffin —above that temperature paraffin alone was used.

The results obtained in the solubility determinations are given in the following table, in which the solubility is expressed in grams of lead nitrate soluble in 100 grams of pyridine. Each figure given is the mean of at least two determinations lying well within the limits of experimental error. The results are shown graphically in Fig. 2, temperatures being charted as abscissas and amounts of lead nitrate, in grams soluble in 100 grams of pyridine, being represented as ordinates.

Analysis of the Solid Phase.—From an inspection of the curve it was evident that in the range of temperature through which these experiments were conducted three solid phases must exist. Analysis of the solids in equilibrium with the pyridine solution were carried out as follows:

The solid in equilibrium at ordinary temperature was filtered off, dried by pressing with filter paper and the percentage of lead determined. The average of several determinations gave 59.11 per cent. $Pb(NO_3)_2$,

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EQUILIBRIUM BETWEEN SATURATED SOLUTION AND SOLID.

Temperature, 0° C.	Grams $Pb(NO_3)_2$ in 100 grams of pyridine.	Temperature, 0° C.	Grams $Pb(NO_3)_2$ in 100 grams of pyridine.
$Pb(NO_3)_2 \cdot 4 C_5H_5N$		$Pb(NO_3)_2 \cdot 3 C_5H_5N$	
—19.4	2.93	59.52	36.70
—14.5	2.14	70.00	47.29
—10.00	1.90	80.00	61.60
0.00	3.54	89.93	90.21
5.4	3.93	94.94	128.06
8.7	5.39		
14.72	6.13	$3Pb(NO_3)_2 \cdot 2C_5H_5N$	
19.97	6.78	99.89	143.36
24.75	8.56	104.90	152.00
30.03	10.98	109.90	163.80
34.97	13.20		
40.03	16.94		
45.00	22.03		
49.97	29.37		

which corresponds to the compound $Pb(NO_3)_2 \cdot 4C_5H_5N$ which contains 51.16 per cent. lead nitrate.

The solid phases at higher temperatures were removed from the liquid and dried in a bath kept at the temperature at which they were separated

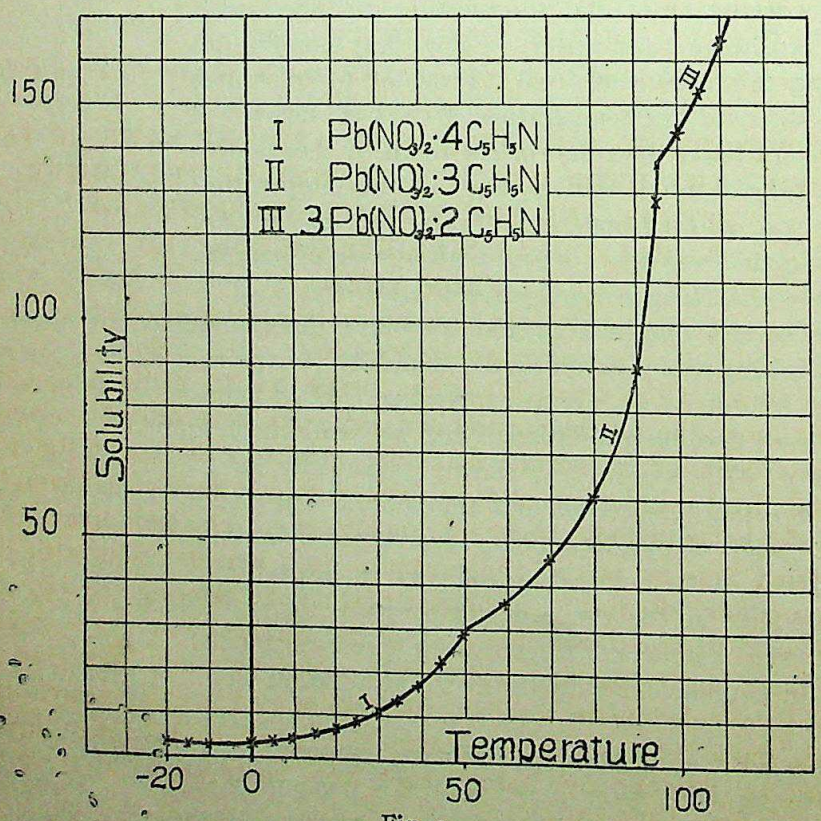

Fig. 2.

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from the liquid. The solid phase between 60° and 95° was found to contain 58.93 per cent. of lead nitrate. The compound $Pb(NO_3)_2.3C_5H_5N$ contains 58.98 per cent. lead nitrate. This is the compound discovered and described by Schmujlow in 1897. Above 95° a compound was found which contained 86.2 per cent. of lead nitrate. This is evidently $3Pb(NO_3)_2.2C_5H_5N$, which contains 86.27 per cent. of lead nitrate.

The transition points may be obtained from the curve. At 51° there is a transition point between $Pb(NO_3)_2.4C_5H_5N$ and $Pb(NO_3)_2.3C_5H_5N$. At 86° there is a transition point between $Pb(NO_3)_2.3C_5H_5N$ and $3Pb(NO_3)_2.2C_5H_5N$.

Summary.

In the foregoing investigation the solubility curve of lead nitrate and pyridine has been established between —19.4 and 110°. The results show that for this range of temperature there are three distinct crystalline compounds of lead nitrate and pyridine in equilibrium with the solution. The three compounds are: $Pb(NO_3)_2.4C_5H_5N$; $Pb(NO_3)_2.3C_5H_5N$; and $3Pb(NO_3)_2.2C_5H_5N$. Of these $Pb(NO_3)_2.4C_5H_5N$ and $3Pb(NO_3)_2.2C_5H_5N$ have hitherto been unknown.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY. No. 192.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE VII. THE DROP WEIGHTS OF SOME OF THE LOWER ESTERS, AND THE SURFACE TENSIONS AND MOLECULAR WEIGHTS CALCULATED FROM THEM.

BY J. LIVINGSTON R. MORGAN AND FREDERICK W. SCHWARTZ.

Received April 19, 1911.

The object of this research was the further testing of the Morgan drop weight apparatus, for the purpose of (1) applying to additional substances the new definition of normal molecular weight in the liquid state; and (2) the direct comparison of the values of surface tension, as found from drop weight, with those from the capillary rise. The main difficulty encountered thus far in the comparison of drop weight results with those from capilliary rise has been the fact that no one agreeing value in many cases could be found from the work of the various observers of capillary rise, their results varying widely. In order that any such variation might be avoided in the capillary rise results used in this research, those liquids, the lower esters, were selected, eight of which have been carefully studied by Ramsay and Aston,[1] each from observations at three tem-

[1] *Z. physik. Chem.*, 15, 98 (1894).

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peratures, in two capillary tubes of differing bore. One great advantage of this form of comparison is that it enables us at the same time to ascertain the degree of accuracy in agreement that may be expected from the capillary rise method under ideal conditions, *i. e.*, where all is identical except the bore of the capillary used, and that it furnishes us with a criterion as to what variation in capillary rise results may be expected when nothing is identical in the work except the name of the liquid used. Another difficulty previously encountered is also done away with in the use of these uniform results, *viz.*, that due to the employment, in the calculation of a different density or rather difference in density as liquid and as vapor, at the same temperature, for the same liquid, for the value of $\gamma = {}^1/_2$ hr. $(d_l - d_v)$ is very decidedly dependent upon that.

The tip used here was one with a straight, sharp, edge, slightly larger than that used by Morgan and Thomssen, and smaller than that of Morgan and Daghlian, and was very approximately 5.65 millimeters in diameter. Owing to the fact that a number of different weighing vessels were used on this apparatus, the total weights of vessel and drops are different in many cases for the same liquid at different temperatures. It is to be remembered here that in the use of this apparatus no comparison can be made between the weights of the 5-drop blanks, except when they refer to the same liquid, at the same temperature. This is due to the fact that the blank is always held on the apparatus, with a drop hanging, for the same length of time that the 25-drop determinations of that liquid at that temperature are allowed to stand; and consequently it always represents the weight of 5 drops, less the loss by evaporation. Two identical weights, then, for the vessel plus 5 drops, for different liquids, at different temperatures, do not necessitate that the weight of 1 drop be the same in both cases; for that which has the greater drop weight, by its loss from evaporation, due to longer standing or higher vapor pressure, will appear decidedly reduced in total weight. It is only when the blanks are considered in connection with the determinations to which they refer that comparable results, *i. e.*, the weight of 1 drop, are obtained.[1]

In Table I are given the experimental results for benzene at two temperatures, together with the values of $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$ and that of k_B calculated from the relationship $w\left(\frac{M}{d}\right)^{\frac{2}{3}} = k_B\,(288.5 - t - 6)$. This is for the purpose of standardizing the tip, the value of k_B found being then used throughout for the calculation of the t_c of the other liquids, and to prove from its constancy, at various temperatures of observation, in any one

[1] This is complicated further here by the fact that a cork stopper was used in the weighing vessel in all the cases given with a weight less than 10 grams; and the cork, although constant in weight for each determination, was not the same throughout.

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case, that the molecular weight of that liquid is normal, *i. e.*, is the same as a liquid as it is as a gas.

In Table II are given the experimental, as well as the derived values for pyridine, which will serve as a preliminary test of the accuracy of the constant of standardization, k_B, of the tip. As will be observed, this value of k_B leads to a value of $t_c = 346.85°$, in place of 346.6°, as calculated by Morgan from the results of Morgan and Higgins. From this result we may regard the value of k_B as satisfactory.

TABLE I.—BENZENE; M = 78; $t_c = 288.5°$.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10°	7.6515		7.0063		
	7.6516	7.6515	7.0062	7.0063	32.260
	7.6515		7.0064		
	7.6514		7.0063		
40.7	11.0195		10.4610		
	11.0194		10.4612		
	11.0194	11.0194	10.4611	10.4611	27.915
	11.0193		10.4611		

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	k_B.
10°	0.88956	32.260	636.72	2.3374
40.7	0.85683	27.915	564.90	2.3372

Av. $k_B = 2.3373$

TABLE II.—PYRIDINE; M = 79; $t_c = 346.6°$.[1]

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop, Mg.
0°	8.5643		7.6986		
	8.5642	8.5643	7.6984	7.69847	43.292
	8.5643		7.6984		
	8.5644		7.6985		
34.25	11.7086		10.9472		
	11.7084		10.9474		
	11.7085	11.7086	10.9475	10.9473	38.065
	11.7087		10.9472		
	11.7088		10.9472		

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c calc. from k_B.
0.1°	1.0014	43.292	796.31	346.8°
34.25	0.9672	38.065	716.58	346.9°

In Tables III to XIII are given the experimental values of the new liquids studied, *viz.*, methyl formate, ethyl formate, propyl formate,

[1] See No. IV of this series.

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amyl formate, methyl acetate, ethyl acetate, propyl acetate, methyl propionate, ethyl propionate, methyl isobutyrate, and methyl butyrate. These, with the exception of the amyl formate, which was obtained from Eimer & Amend, and though purified before the determination, cannot be considered as satisfactory, were prepared especially for the work by the Hoffman & Kropff Chemical Company, and used as received. It will be noted here that the maximum variation from the mean, *i. e.*, where the "25" determinations differ by 0.4 mg. and the blanks also differ by 0.03, amounts to only about 0.05 per cent., the average variation being much less. This, naturally, is simply the variable error, the absence of a constant error in any one case being shown better perhaps by the results given later:

TABLE III.—METHYL ISOBUTYRATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10°	9.8776		9.3452		
	9.8775		9.3450		
	9.8773	9.8775	9.3451	9.34512	26.619
	9.8776		9.3452		
33.87	9.8085		9.3336		
	9.8084		9.3337		
	9.8083	9.80845	9.3335	9.33366	23.740
	9.8083		9.3338		
	9.8087		9.3338		
60.1	9.7385		9.3260		
	9.7386	9.73862	9.3261	9.32594	20.634
	9.7387		9.3259		
	9.7387		9.3259		
	....		9.3259		

TABLE IV.—ETHYL PROPIONATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10°	6.7887		6.2480		
	6.7888	6.78875	6.2480	6.2479	27.043
	6.7888		6.2478		
	6.7887		6.2478		
33.89	9.8185		9.3356		
	9.8187	9.8186	9.3356	9.33557	24.152
	9.8186		9.3355		
	9.8186		9.3356		
59.15	10.7920		10.3682		
	10.7921	10.7920	10.3682	10.36812	21.194
	10.7920		10.3681		
	10.7919		10.3680		

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TABLE V.—METHYL PROPIONATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop Mg.
10°	6.8100		6.2513		
	6.8102	6.81007	6.2513	6.2512	27.944
	6.8100		6.2512		
	6.8101		6.2510		
34.65	10.9364		10.4426		
	10.9362	10.9363	10.4425	10.44257	24.687
	10.9363		10.4425		
	10.9363		10.4427		
59.75°	10.8000		10.3701		
	10.8002		10.3703		
	10.8002	10.8001	10.3702	10.37012	21.499
	10.8001		10.3699		
	10.8000		.....		

TABLE VI.—ETHYL FORMATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	8.1827		7.6228		
	8.1827	8.18275	7.6230	7.62298	27.989
	8.1828		7.6230		
	8.1828		7.6231		
6.	8.3243		7.7809		
	8.3243	8.3243	7.7810	7.7809	27.170
	8.3242		7.7808		
	8.3244		7.7809		
10	8.3355		7.8028		
	8.3358	8.33567	7.8030	7.80292	26.638
	8.3357		7.8029		
	8.3357		7.8030		
17	8.2888		7.7751		
	8.2886	8.2888	7.7752	7.7752	25.680
	8.2889		7.7753		
	8.2889		7.7752		
33.95°	10.9059		10.4381		
	10.9058	10.9059	10.4382	10.43815	23.388
	10.9059		10.4380		
	10.9060		10.4383		

TABLE VII.—METHYL ACETATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	8.2152		7.6292		
	8.2151		7.6291		
	8.2150	8.21512	7.6291	7.6291	29.301
	8.2152		7.6290		

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TABLE VII (*Continued*).

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10	6.8070		6.2510		
	6.8069	6.80687	6.2509	6.25085	27.801
	6.8068		6.2508		
	6.8068		6.2507		
34.2	8.2822		7.7990		
	8.2823	8.28227	7.7991	7.79907	24.160
	8.2822		7.7991		
	8.2824		7.7991		

TABLE VIII.—PROPYL ACETATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	8.1884		7.6199		
	8.1885	8.18855	7.6198	7.6199	28.433
	8.1886		7.6199		
	8.1887		7.6200		
34.6	7.4602		6.9773		
	7.4603		6.9773		
	7.4602	7.46022	6.9772	6.97727	24.148
	7.4602		6.9773		
60.1	11.1213		10.6972		
	11.1216	11.12147	10.6973	10.69732	21.208
	11.1215		10.6974		
	11.1215		10.6974		

TABLE IX.—METHYL BUTYRATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10°	8.3627		7.8043		
	8.3626	8.36262	7.8042	7.80422	27.920
	8.3627		7.8042		
	8.3625		7.8042		
34.8	8.2869		7.7885		
	8.2867	8.2868	7.7885	7.7885	24.915
	8.2868		7.7885		
	8.2868		7.7885		
59.85	8.2217		7.7824		
	8.2218		7.7824		
	8.2217	8.22168	7.7824	7.7824	21.964
	8.2216		7.7824		
	8.2216		....		

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TABLE X.—PROPYL FORMATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	7.5616		6.9895		
	7.5615	7.56152	6.9895	6.98945	28.604
	7.5615		6.9894		
	7.5615		6.9894		
5.4	8.3638		7.8050		
	8.3639	8.36382	7.8050	7.8050	27.941
	8.3638		7.8050		
	8.3638		7.8050		
10	8.3492		7.8026		
	8.3494		7.8027		
	8.3494	8.34935	7.8027	7.80262	27.337
	8.3494		7.8025		
17	8.3283		7.7992		
	8.3284	8.32835	7.7992	7.7992	26.458
	8.3284		7.7992		
	8.3283		7.7992		
34.75	7.4595		6.9733		
	7.4593	7.45942	6.9735	6.97347	24.298
	7.4594		6.9736		
	7.4595		6.9735		
60.3	7.3903		6.9620		
	7.3903		6.9619		
	7.3902	7.3903	6.9619	6.96192	21.419
	7.3905		6.9619		
	7.3902		....		

TABLE XI.—METHYL FORMATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	8.2323		7.6345		
	8.2323	8.23237	7.6345	7.63452	29.893
	8.2325		7.6345		
	8.2324		7.6346		
6.7	8.3898		7.8125		
	8.3898		7.8126		
	8.3897	8.38975	7.8125	7.81255	28.860
	8.3897		7.8126		
10	7.5554		6.9906		
	7.5553		6.9906		
	7.5554	7.5554	6.9904	6.99055	28.243
	7.5555		6.9906		
16.4	8.3485		7.8013		
	8.3486	8.3485	7.8013	7.8013	27.360
	8.3485		7.8013		
	8.3484		7.8013		
27.82	8.3071		7.7948		
	8.3072	8.30717	7.7949	7.7949	26.614
	8.3071		7.7949		
	8.3073		7.7950		

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TABLE XII. AMYL FORMATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10°	8.3484		7.7993		
	8.3486		7.7992		
	8.3485	8.3485	7.7992	7.79922	27.464
	8.3485		7.7992		
35	8.2813		7.7875		
	8.2813	8.28135	7.7875	7.7875	24.693
	8.2814		7.7875		
	8.2814		7.7875		
60.1	8.2176		7.7796		
	8.2176		7.7796		
	8.2177	8.21767	7.7797	7.7796	21.904
	8.2177		7.7795		
	8.2177		....		

TABLE XIII.—ETHYL ACETATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	7.5421		6.9834		
	7.5420	7.5421	6.9834	6.9833	27.940
	7.5421		6.9832		
	7.5422		6.9832		
34.6	7.4442		6.9767		
	7.4443	7.44424	6.9768	6.97674	23.375
	7.4443		6.9767		
	7.4442		6.9769		
60.5	7.4442		6.9766		
	7.3658		6.9646		
	7.3659	7.3659	6.9647	6.96462	20.064
	7.3659		6.9646		
	7.3660		6.9646		

In Tables XIV to XXIV, inclusive, are given the derived values $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$, t_c, and γ (surface tension) calculated from the above experimental results, together with the corresponding quantities from the capillary rise results of Ramsay and Aston and others.

The densities employed here, except those for amyl formate, which were partly extrapolated from those used by Homfray and Guye,[1] were found by plotting the results of Young.[2]

The t_c values from drop weight as given are all calculated by aid of the value of k_B found above for benzene, *viz.* 2.3373, in the equation $w\left(\frac{M}{d}\right)^{\frac{2}{3}} = 2.3373(t_c-t-6)$, while those from capillary rise are obtained by the use of the specific value of k_B found from the work of the investi-

[1] *J. chim. phys.*, 1, 505–44 (1904).
[2] *J. Chem. Soc.*, 1893, 1191–1262.

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gator in question on benzene; or by use of the Ramsay and Shields' constant when the observer calibrated the bore of his capillary by aid of their benzene values. Naturally, here, the comparison of drop weight with surface tension from capillary rise, by aid of 2 equations like the above, is made by the identity in the values of t_c found, for since M is the same in both, while d is the same function of the temperature in each, identity in the t_c shows that *at the same temperature* we would have the relation $\gamma : w :: k_B' : k_B$. When the comparison itself is made at the same temperature, t, the above relationship is, of course, self-evident, since M, d, t and 6 are all alike, so that when *the t_c's are also identical, the drop weight in milligrams is related to the surface tension in dynes per centimeter, as the respective k_B values, i. e.*, at the same temperature $w : \gamma :: k_B : k_B'$.

One difficulty with respect to this indirect comparison of drop weight and surface tension is that the densities used may not be the same, or the same function of the temperature; while another is that the t_c found for the liquid in question increases or decreases with the temperature. The simplest way to avoid these difficulties is to make a direct comparison of the surface tensions themselves, at the same temperature. In the second part of each of the following tables will be found the surface tensions as observed directly from the capillary rise, together with those values, interpolated or extrapolated from the surface tensions calculated from the drop weight, at each temperature of observation, by aid of the equation $\gamma = w\frac{k_B}{2.3373}$ dynes, where the value of k_B depends upon the observer of capillary rise. The differing values of γ obtained by use of the various k_B values would best, perhaps ultimately, be made uniform by the use of a value of k_B from capillary rise which is the average of all those which have been observed. This would have a value then of about 2.1111, differing from that of Ramsay and Shields (2.1012) by 0.47 per cent., and from that of Ramsay and Aston (2.1211) by 0.5 per cent., while it is practically identical with that of Renard and Guye (2.1108).

All extrapolated values in the tables are marked with *.

In Table XXV are given the values of t_c for the above liquids, as found from the modified Walden relationship,

$$t_c = \text{constant}\,\frac{\alpha' + \alpha''}{\alpha'\alpha''},$$

where α' and α'' are found from the equations

$$w_t = w_0(1 - \alpha' t),$$

$$\text{and } v_t = \frac{w_t}{d_t} = v_0(1 - \alpha'' t),$$

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using the values at the extremes of temperature in order that they may be as free from error as possible. The value of the constant here, as in the previous papers, is that which is found necessary to give t_c for benzene the value 288.5°:

TABLE XIV.—METHYL ISOBUTYRATE; M = 102.08; t_c obs. = 267.6°.

t.	d.	w. Mgs.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{k_{R\&A}}{2.3373}\right)$. Dynes.	$\gamma\left(=w\frac{k_{R\&G}}{2.3373}\right)$. Dynes.
10.0°	0.90033	26.619	623.57	*282.8*	24.158	24.040
33.9	0.87328	23.740	567.55	*282.7*	21.545	21.440
60.1	0.84295	20.634	505.06	*282.2*	18.726	18.634

Ramsay and Aston; k_B = 2.1212.

t.	$\gamma = 0.01708$ cm. $\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma = 0.01046$ cm. $\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	563.6	*281.7*	563.0	*281.4*
46.2	487.3	*281.9*	486.1	*281.4*
78.2	415.0	*279.8*	415.1	*279.9*

Renard and Guye; k_B = 2.1108.

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.5°	563	*283.2*	55.0	467	*282.2*
30.5	519	*282.4*	75.0	422	*280.9*
41.0	496	*282.0*	86.6	396	*280.2*

Surface Tensions.

t.	γR & A.		γM & S from $w\frac{2.1212}{3.3373}$.
10.0°	24.11	24.08	24.16
46.2	20.29	20.04	20.22
78.2	16.70	16.64	16.78*

	γR & G.	γM & S from $w\frac{2.1108}{2.3373}$.
10.5°	24.06	24.03
30.5	21.82	21.81
41.0	20.63	20.68
55.0	19.18	19.18
75.0	17.02	17.04*
86.6	15.78	15.80*

TABLE XV.—ETHYL PROPIONATE; M = 102.08; t_c obs. = 272.9°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1212}{2.3373}\right)$.
10.0°	0.90106	27.043	633.16	*286.9*	24.543
33.9	0.87435	24.152	576.93	*286.7*	21.919
59.2	0.84502	21.194	517.92	*286.8*	19.234

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Table XV (*Continued*).

Ramsay and Aston; $k_B = 2.1212$.

t.	$r = 0.01708$ cm. $r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$r = 0.01046$ cm. $r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	574.0	*286.6*	576.2	*287.6*
46.2	496.1	*286.1*	496.9	*286.5*
78.2	428.1	*286.0*	427.8	*285.9*

Surface Tensions.

t.	γ R & A.		γ M & S from $w\frac{2.1212}{2.3373}$.
10.0°	24.57	24.67	24.54
46.2	20.58	20.62	20.60
78.2	17.24	17.22	17.20*

TABLE XVI.—METHYL PROPIONATE; M = 88.06; t_c obs. = 257.4°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1212}{2.3373}\right)$.
10.0°	0.92678	27.944	582.31	*265.1*	25.360°
34.7	0.89758	24.687	525.14	*265.4*	22.405
59.8	0.86692	21.499	468.04	*266.1*	19.511

Ramsay and Aston; $k_B = 2.1212$ cm.

t.	$r = 0.01708$ cm. $r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$r = 0.01046$ cm. $r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	524.3	*263.2*	530.2	*266.0*
46.2	447.3	*263.1*	450.2	*264.4*
78.2	378.8	*262.8*	381.9	*264.2*

Surface Tensions.

t.	γ R & A.		γ M & S from $w\frac{2.1212}{2.3373}$.
10.0°	25.23	25.51	25.36
46.2	20.85	20.98	21.08
78.2	17.11	17.26	17.30*

TABLE XVII.—ETHYL FORMATE; M = 74.08; $t_c = 235.2°$.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1212}{2.3373}\right)$.
0.1°	0.94697	27.989	511.82	*225.1*	25.401
6.0	0.93958	27.170	499.44	*225.7*	24.658
10.0	0.93458	26.638	491.41	*226.3*	24.175
17.0	0.92618	25.680	476.59	*226.9*	23.306
34.0	0.90418	23.388	441.07	*228.7*	21.226

Ramsay and Aston; $k_B = 2.1212$.

t.	$r = 0.01843$ cm. $r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$r = 0.01046$ cm. $r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	443.5	*225.1*	446.0	*226.3*
46.5	371.5	*227.6*	375.5	*229.5*
78.5	309.2	*230.3*	309.1	*230.3*

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TABLE XVII (*Continued*).

Surface Tensions.

t.	γR & A.		γM & S from $w\frac{2.1212}{2.3373}$.
10.0°	24.08	24.22	24.18
46.5	19.50	19.71	19.68*
78.5	15.68	15.68	15.73* (Extrapolated through 44.5°)

TABLE XVIII.—METHYL ACETATE; M = 74.05; t_c obs. = 233.7°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1212}{2.3373}\right)$.
0.1°	0.95900	29.301	531.23	*233.2*	26.592
10.0	0.94652	27.801	508.54	*233.6*	25.231
34.2	0.91491	24.160	452.19	*233.7*	21.926

Ramsay and Aston; k_B = 2.1212.

t.	γ = 0.01843 cm. $\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	γ = 0.01046 cm. $\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	462.8	*234.2*	459.9	*232.8*
46.2	383.9	*233.2*	387.2	*234.7*
78.3	318.2	*234.2*	319.5	*234.9*

Surface Tensions.

t.	γR & A.		γM & S from $w\frac{2.1212}{2.3373}$.
10.0°	25.22	25.06	25.23
46.2	20.32	20.49	20.29*
78.3	16.28	16.35	15.89 (Extrapolated through 44.1°)

TABLE XIX.—PROPYL ACETATE; M = 102.08; t_c obs. = 276.2°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1212}{2.3373}\right)$.
0.1°	0.91000	28.433	661.20	*289.0*	25.804
34.6	0.87229	24.148	577.63	*287.7*	21.915
60.1	0.84345	21.208	518.81	*288.1*	19.247

Ramsay and Aston; k_B = 2.1212.

t.	γ = 0.01708 cm. $\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	γ = 0.01046 cm. $\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	580.2	*289.5*	582.0	*290.4*
46.2	503.0	*289.3*	502.2	*289.0*
78.2	431.0	*287.4*	432.3	*288.0*

Surface Tensions.

t.	γR & A.		γM & S from $w\frac{2.1212}{2.3373}$.
10.0°	24.80	24.88	24.72
46.2	20.86	20.84	20.77
78.2	17.35	17.33	17.27*

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TABLE XX.—METHYL BUTYRATE; M = 102.08; t_c obs. = 281.3°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c	$r\left(=w\frac{2.1212}{2.3373}\right)$.
10.0°	0.90925	27.920	649.76	*294.0*	25.340
34.8	0.88175	24.915	591.82	*294.0*	22.610
59.9	0.85375	21.964	533.07	*294.0*	19.930

Ramsay and Aston; k_B = 2.1212.

	r = 0.01843 cm.		r = 0.01046 cm.	
t.	$r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	595.0	*296.5*	591.7	*295.0*
46.2	514.5	*294.8*	511.8	*293.5*
78.2	446.9	*294.9*	444.4	*293.7*

Surface Tensions.

t.	rR & A.		rM & S from $w\frac{2.1212}{2.3373}$
10.2°	25.63	25.50	25.34
46.2	21.50	21.39	21.40
78.2	18.15	18.05	17.98*

TABLE XXI.—PROPYL FORMATE; M = 88.06; t_c obs. 264.9°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$r\left(=w\frac{2.1212}{2.3373}\right)$.
0.1°	0.92850	28.604	594.88	*260.6*	25.960
5.4	0.92251	27.941	583.60	*261.1*	25.358
10.0	0.91726	27.337	573.16	*261.2*	24.809
17.0	0.90909	26.458	558.05	*261.7*	24.012
34.8	0.88873	24.298	520.29	*263.9*	22.051
60.3	0.85837	21.419	469.39	*267.1*	19.439

Ramsay and Aston; k_B = 2.1212.

	r = 0.01843 cm.		r = 0.01046 cm.	
t.	$r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	523.6	*262.8*	524.4	*263.2*
46.5	446.3	*262.9*	447.1	*263.3*
78.3	387.0	*266.8*	385.2	*265.9*

Surface Tensions.

t.	rR & A.		rM & S from $w\frac{2.1212}{2.3373}$.
10.0°	25.02	25.06	24.8[illegible]
46.5	20.67	20.71	20.53
78.3	17.52	17.44	17.61*

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TABLE XXII.—METHYL FORMATE; M = 60.03; t_c obs. 214°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c	$\gamma\left(w=\frac{2.1012}{2.3373}\right)$.
0.1°	1.00300	29.893	457.39	*201.8*	26.873
6.7	0.99354	28.860	444.38	*202.8*	25.945
10.0	0.98892	28.243	436.23	*202.6*	25.390
16.4	0.97943	27.360	425.32	*204.4*	24.596
27.8	0.96320	25.614	402.64	*206.1*	23.027

Ramsay and Shields; k_B = 2.1012.

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
20°	383.9	*208.7*	50°	322.6	*209.5*
30	363.7	*209.1*	60°	302.5	*210.0*
40	343.2	*209.3*	70°	282.7	*210.5*

Surface Tensions.

t.	γR & S.	γM & S from $w\frac{2.1012}{2.3373}$.
20°	24.64	24.11
30	23.09	22.72*
40	21.56	21.34*
50	20.05	19.95*
60	18.58	18.57*
70	17.15	17.19* (Extrapolated through 43.2°)

TABLE XXIII.—AMYL FORMATE; M = 116.1; t_c obs. = 304.6°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1012}{2.3373}\right)$.
10.0°	0.8882	27.464	706.26	*318.6*	24.686
35.0	0.8682	24.693	645.73	*317.3*	22.199
60.1	0.8420	21.904	584.62	*316.2*	19.691

Homfray and Guye; k_B = 2.1012.[1]

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
43.8°	569.5	*320.8*
77.8	497.8	*320.7*
109.2	432.2	*320.9*

Surface Tensions.

t.	γH & G.	γM & S from $w\frac{2.1012}{2.3373}$.
43.8°	21.64	21.51
77.8	18.40	18.12*
109.2	15.52	15.05* (Extrapolated through 49.1°)

TABLE XXIV.—ETHYL ACETATE; M = 88.06; t_c obs. = 250.1°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1061}{2.3373}\right)$.
0.1°	0.92421	27.940	582.86	*255.4*	25.175
34.6	0.88277	23.375	502.77	*255.7*	21.062
60.5	0.85019	20.064	442.51	*255.8*	18.078

[1] Benzene values not given, but as authors used capillary of Guye and Baud who calibrated the bore from the benzene results of Ramsay and Shields, 2.1012 is assumed as correct.

[2] Average of 2.1108 and 2.1012 used for finding γ for the comparison.

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Table XXIV (*Continued*).

Ramsay and Shields; $k_B = 2.1012$.

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
20°	500.7	*264.3*	100°	321.7	*259.1*
80	367.2	*260.8*	110	299.0	*258.3*
90	344.4	*259.9*	120	277.0	*257.9*

Guye and Baud; $k_B = 2.1012$.

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
9.5°	519.6	*262.8*	....	....	....
55.6	413.0	*258.2*	....	....	....
77.0	373.0	*260.5*	....	....	....

Renard and Guye; $k_B = 2.1108$.

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
12.9°	509	*260.0*	55.0°	418.0	*259.0*
31.3	470	*260.0*	65.9	394.0	*258.6*
46.9	437	*259.9*	73.5	381.0	*260.0*

Surface Tensions.

t.	γR & S.	γG & B.	γR & G.	γM & S.
10°	24.81*	24.64	24.50	24.00
20	23.60	23.36	23.27	22.82
30	22.39	22.08	22.04	21.64
40	21.18	20.80	20.89	20.44
50	19.97	19.52	19.71	19.29
70	17.55	17.35	17.39	16.99*
80	16.32	16.32*	16.47*	15.84*

TABLE XXV.

$t_c = \text{constant}\ \frac{\alpha' + \alpha''}{\alpha'\alpha''}$ [1].

Liquid.	α'.	α''.	t_c.	t_c from k_B.
Pyridine	0.003534	0.002624	348.0	346.9
Methyl isobutyrate	0.004295	0.003321	279.9	282.6
Ethyl propionate	0.004211	0.003231	286.7	286.8
Methyl propionate	0.004426	0.003443	270.7	265.5
Methyl acetate	0.005143	0.003979	233.7	233.5
Propyl acetate	0.004233	0.003244	285.5	288.3
Methyl butyrate	0.004100	0.003148	294.5	294.0
Ethyl acetate	0.004665	0.003630	256.8	255.6
Ethyl formate	0.004847	0.003681	250.6	225.1–228.7
Amyl formate	0.003884	0.003070	305.7	318.6–316.2
Propyl formate	0.004171	0.003060	297.0	260.6–257.1
Methyl formate	0.005165	0.003888	234.4	201.8–206.1

[1] The values for benzene are $\alpha' = 0.004203$ and $\alpha'' = 0.003201$, from which, taking $t_c = 288.5°$, the constant is found to be 0.5243.

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Discussion of the Results.

Taking up the liquids in the order they are given in the tables, we find for methyl isobutyrate (XIV) that the calculated value of t_c is constant from drop weight, but has a slight trend downward according to the results from capillary rise, though it must be conceded that the numbers by the latter method are hardly consistent, for Renard and Guye find a sudden break between 55° and 75° of 1.3°, although from 30.5° to 35° there is only one of 0.2°. In other words, it would seem that there is some error in the capillary rise, as judged from the t_c value, which occurs between 55° and 75° for Renard and Guye, and between 46.2° and 78.2° for Ramsay and Aston. This may be very well due to the use of density values which are not quite consistent at the high and the low temperatures. Comparison of the surface tension values as calculated by the two methods, where those from drop weight are free from any effect of density, shows an excellent agreement with the results of Ramsay and Aston, and one that is truly remarkable, even to the extrapolated values, with those of Renard and Guye.

With ethyl propionate the agreement in the values of t_c, which is constant by both methods, is excellent, while the drop weight surface tensions are found to lie between the values found by Ramsay and Aston in two capillaries of differing bore.

The t_c values for methyl propionate by drop weight may be considered as constant, the variation, which is not excessive, being due probably to the density. If a trend is assumed here it is certainly in the opposit direction from that found from the capillary rise. The t_c values in one of Ramsay and Aston's tubes is also practically constant, but is slightly smaller throughout than the drop weight value, while the other shows a higher value even than that, at 10°, and then remains constant at a value midway between that of the other and the drop weight. The comparison of the surface tension values from the two methods shows an agreement which is excellent.

With ethyl formate the t_c values show an increase with the temperature throughout, the values from the two methods being practically identical when with the same density values the t_c's are calculated from the surface tension values of drop weight. These latter, except that extrapolated through 44.5°, lie between the surface tensions from the two tubes of Ramsay and Aston. We shall return to the trend in the t_c values again.

Methyl acetate is the only liquid among those investigated, which leads to a t_c value in agreement with the observed critical temperature, and is found both by drop weight and capillary rise, for the mean of all the Ramsay and Aston values is 234°, as compared with 233.5° by drop weight, and 233.7° observed directly. The surface tensions here also

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agree in an extremely satisfactory manner, including one of the extrapolated values, although the other, extrapolated through 44.1°, does not. It is to be remembered here that the drop weight surface tension is one that at 78.3° with the constant 2.1212 would still give 233.5°, while the capillary rise value would lead to a higher result.

In the case of propyl acetate, the slight variation in the t_c values is probably due to the density used, and is not thought to indicate a trend. The means of all the Ramsay and Aston values is 288.9°, while that from the drop weight is 288.3°. The surface tensions from drop weight are very slightly smaller throughout than those from capillary rise, but the difference is less than that often noticed between the values from the two tubes of Ramsay and Aston, which should be identical in result.

In the case of methyl butyrate the drop weight t_c is identical at all three temperatures, while a slight variation is shown by the capillary rise method, the results of which differ, when found from the different tubes, by 1°. Considering all this as due to variable error in the capillary rise values, we find the mean t_c to be 294.7°, as compared to the constant 294° from drop weight. The surface tensions here, except for 10°, where the capillary rise values differ considerably among themselves, is very good indeed.

Propyl formate shows an increase in t_c with the temperature by both drop weight and capillary rise, the values from drop weight not agreeing very well, either with respect to t_c or to surface tension, with those from capillary rise. The behavior of this liquid was found to be striking, in that when heated for a few hours at 60°, a reversible reaction appears to take place which increases the drop weight, when it is determined again at 10°. Thus heating for 2 hours, then allowing the liquid to cool naturally, and determining the drop weight at 10°, a value 27.434 is obtained, as against 27.337 for the unheated sample. After standing for 16 hours, this weight is reduced to 27.430, and after 10 days to 27.366. Heating to 60° and cooling suddenly, as in a distillation, leads to a value of 27.337, *i. e.*, one identical with that of an unheated sample. Since nothing else in the behavior of the liquid indicated a reason for this, it is assumed that a definit reaction takes place on raising the temperature, which reverses slowly, unless the cooling is very rapid, when it returns at once to its original state. Using the value at 10° found after heating, the drop weight t_c would be increased to 262.2, which is in better agreement with one of the Ramsay and Aston values. As far as can be found from the paper, Ramsay and Aston always worked at the higher temperatures first, gradually lowering the temperature by reducing the pressure over the boiling liquid which heated the bath. This would account for their higher values at the low temperature—for the actual state at the higher temperature would then persist at the lower one. With the drop weight,

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on the other hand, the weight at the lower temperature was always determined from a sample, which, if it had been heated, had returned to its original state.

Methyl formate is a liquid which had been investigated by Ramsay and Shields, and was consequently not studied by Ramsay and Aston. Here again a value of t_c increasing with the temperature is observed by both methods. The drop weight surface tensions here at the low temperatures do not agree well with those from the capillary rise, but the agreement becomes better and better as the temperature of observation increases, even though all but one of the drop weight values are extrapolated, until the agreement is perfect. This would indicate a behavior similar to that of propyl formate, the low values of the capillary rise being influenced by the persistence of the high temperature conditions, while the drop weight is unaffected by it. When the possibility of this effect disappears, the two methods lead to identical results. Here the lower values by drop weight, being smaller than they should be, while that at 27.8° is less affected, would produce a curve which when combined would naturally eliminate at the higher temperatures the effect of the heat reaction noticeable at the low temperatures.

Amyl formate has been investigated only by Homfray and Guye. The sample used here was probably not pure, and certainly the densities employed were not satisfactory, as the three values given by Homfray and Guye did not allow an accurate extrapolation. As will be observed, the t_c values from capillary rise are very constant, while those from drop weight decrease slightly, and are smaller throughout. This may, of course, be due either to the effect of density or to an impurity. The surface tensions differ as do the values of t_c; this would seem to indicate that the purity of the liquid used for the drop weight is questionable. It can be concluded there that through no fault of the drop weight method, the results from capillary rise are probably the more correct.

For ethyl acetate a constant t_c is found both from drop weight and from capillary rise as found by Guye and Baud and Renard and Guye, although the values differ considerably. Ramsay and Shields find a downward trend. The difference in the three values of surface tension from capillary rise is best shown perhaps when all are calculated to the same temperature. It will be observed here that it is at the low temperatures especially that the results of the 3 observers of capillary rise differ, differences of 1 per cent. and more being common. It is unfortunate that this liquid was not investigated by Ramsay and Aston in their two tubes. As it is, there is no apparent reason why drop weight and capillary rise should differ as they do, especially in view of the other excellent agreements. One thing is certain from the constant t_c, both from drop weight and from capillary rise, *viz.*, ethyl acetate is to be regarded as normal in molecular weight, *i. e.*, it is non-associated.

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It will be seen from the above that *according to the new definition of normal molecular weight the following liquids are to be regarded as normal and non-associated: methyl isobutyrate, ethyl propionate, methyl propionate, methyl acetate, propyl acetate, methyl butyrate, amyl formate (from capillary rise values of t_c), and ethyl acetate.* Ethyl formate, methyl formate, and propyl formate do not satisfy this definition and consequently are not to be considered as normal; but their behavior may in all cases be due to such a reversible reaction as is indicated above in the case of propyl formate when heated.

A sample of amyl formate was heated to 230° in the presence of mercury in a closed tube for 4 hours, *i. e.*, submitted to somewhat the same conditions that would hold during an observation of the critical temperature. On opening the tube considerable pressure was observed, while the liquid, which had a somewhat different odor, showed a drop weight at 10° of 27.309, as compared to the value 27.464, obtained before heating. This, of course, is not to be considered as the opposit behavior to that of propyl formate when heated to 60°, for here an actual decomposition takes place. If this decomposition always takes place in the determination of the critical temperature, it would account for the differences between the 304° observed and the fictitious critical temperature, t_c, found above, *viz.*, 321°.

Table XXV gives the results of t_c calculated by aid of the Walden relationship $t_c = \text{constant} \frac{\alpha' + \alpha''}{\alpha' \alpha''}$, where the values of α' and α'' are found from the equations $w_t = w_0(1 - \alpha' t)$ and $v_t = \frac{w_t}{d_t} = v_0(1 - \alpha'' t)$. It will be observed here that the agreement is as good as can be expected (remembering the multiplication of error in finding α' and α''), *i. e.*, in all cases where the t_c found from k_B is constant.

Conclusions.

The results of this investigation may be summarized as follows:

1. It is shown by aid of the new definition of normal molecular weight in the liquid state, *i. e.*, the finding of a calculated value of t_c from the equation $w\left(\frac{M}{d}\right)^{\frac{2}{3}} = k_B(t_c - t - 6)$, which does not vary with the temperature of observation, using in all cases the value of k_B found for benzene and taking $t_c = 288.5°$, that methyl acetate, ethyl acetate, propyl acetate, methyl butyrate, methyl isobutyrate, methyl propionate, ethyl propionate, and amyl formate are normal in molecular weight, *i. e.*, are non-associated.

2. It is found that only in the case of methyl acetate does the calculated t_c agree with the observed critical temperature, the fictitious critical temperatures, t_c, being the higher in all the others except ethyl, methyl

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and propyl formates, where it approaches the observed value with increased temperature.

3. Methyl, ethyl and propyl formates show varying values of t_c with the temperature. In one of these (it is probably true for all) it is shown that apparently a reaction which is reversible is caused by increased temperature, which can be reversed by sudden cooling, but which persists on slow cooling, leading at the lower temperatures to a higher drop weight (and also t_c) than the unheated sample. It is only after some days that this heated sample again returns to its original, unheated value. This reaction is probably what causes the drop to be heavier than it should be at the higher temperature, and to lead to the value of t_c which is larger at 60° than at 0° by 6° in the maximum. We cannot say then that these three formates are either associated or normal; but simply that increased temperature causes a reaction of an unknown nature to take place.

4. Surface tensions in dynes per centimeter, calculated from the drop weight by multiplication by the ratio of the benzene constant for capillary rise to that for drop weight, are found to agree exceedingly well with those of Ramsay and Aston. The agreement of methyl formate with the figures of Ramsay and Shields is not so good, nor that of amyl formate with those of Homfray and Guye (although this is probably due to the impurity of the sample used with drop weight), while the values for ethyl acetate vary considerably from those of the workers on capillary rise, although these do not agree well among themselves.

5. The values of t_c calculated from the modified Walden relationship agree as well with those from the k_B formula as can be expected, except for ethyl, methyl and propyl formates, where since the k_B values are variable, no agreement can be expected.

LABORATORY OF PHYSICAL CHEMISTRY.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 194.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. VIII. THE RELATIONSHIP EXISTING BETWEEN THE WEIGHT OF THE DROP, THE DIAMETER OF THE TIP FROM WHICH IT FALLS, AND THE SURFACE TENSION OF THE LIQUID.

BY J. LIVINGSTON R. MORGAN AND JESSIE V. CANN.

Received May 6, 1911.

It has been shown in previous papers that *for any one tip the laws of Tate, viz.: the weight of a falling drop is proportional to the surface tension of the liquid; and the weight of the drop decreases with increased temperature,* are true. The object of this paper is to present the results of a study

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of Tate's other law—*that the weight of a falling drop is proportional to the diameter of the tip from which it falls.*

In Table I are given the experimental results obtained with the Morgan drop weight apparatus, at the constant and uniform temperature of 27.8° ± 0.02°, using 16 tips, from 3.05 to 7.86 mm. in diameter, the liquids being carbon tetrachloride, ether, benzene, pyridine, and quinoline. The benzene here was Kahlbaum's "thiophene free," the pyridine, ether and quinoline from the same source, but the two latter were always freshly distilled just before the determination, while the carbon tetrachloride was from Baker, and also freshly distilled.

TABLE I.—DROP WEIGHTS IN MILLIGRAMS.[1]

Diameter of tip. Mm.	Benzene.	Quinoline.	Pyridine.	Ether.	Carbon tetrachloride.
3.05	17.355	28.063	22.699	9.843	15.515
3.93	21.564	34.572	28.324	12.284	19.664
4.00	21.934	35.165	28.811	12.497	19.998
4.51	24.268	38.487	31.811	13.814	22.438
4.70	25.245	.....	.....	.....	23.525
4.98	26.753	42.480	35.137	15.243	25.066
5.31	28.526	.....	.....	.....	27.004
5.50	29.528	46.916	38.762	16.826	28.224
5.50	29.532	46.920	38.766	16.827	.....
5.69	30.532	48.540	40.074	17.501	29.556
5.85	31.349	49.692	41.197	18.004	30.698
6.20	33.287	52.680	.....	.....	32.632
6.55	35.351	55.698	46.147	20.658	34.672
6.84	37.157	58.111	48.200	21.740	36.620
7.39	40.749	63.124	52.350	24.008	.....
7.86	43.830	67.638	56.079	26.094	.....

The diameters of the above tips were measured by aid of a dividing engine,[2] reading to 0.001 millimeter, each value given in the Table being the mean of a number of measurements, of several diameters; but as the cross-section at the end was never perfectly circular, and in many cases the edges, viewed under the microscope, were not perfectly sharp, the accuracy is not as great as was desired. The results, in general, however, it is thought, are burdened with an error of less than 0.01 mm.

The drops which formed on the three smallest tips were entirely different in appearance, especially toward the end of their life, from what was expected. In place of rising over the edge, as will happen when such

[1] At the suggestion of the Editor the experimental results, consisting of 389 individual determinations, are given in this form. Each of the above values is found from the mean of several 30-drop determinations with the mean of several 5-drop blanks, the extreme variation for the 25 drops being never more than a few tenths of a milligram.

[2] Our thanks are due to Dr. C. C. Trowbridge, of the Department of Physics, who placed at our disposal the dividing engine, and aided us materially in preparing for the measurements.

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a small tube is jarred, and which was expected in these cases, the drop here continued to hang from the edge without any sign of rising above it, so that up to the time when it was somewhat more than half formed, its appearance was similar to a drop hanging from one of the larger tips, such as have been considered in the other papers of this series. Sooner or later, however, as the drop increased in size, *a change in its profile became apparent, the lower part bulging out beyond the limits which would result from a projection of the circumference of the tip, and forming what might be described as a spherical mass of liquid joined to the tube by a column of smaller diameter. There was, however, no rising of the liquid over the edge.* It is probable that with a still smaller tip, the immediate consequence of this formation of a larger mass of liquid at the bottom of the drop would be to force the liquid up and over the edge of the tip, though in these cases no such result was observed.

Naturally if the drop rises over the edges of the tip, the weight falling will be larger than it should be, for the area from which it falls would be increased by an amount which depends upon the surface tension of the liquid, and hence is not uniform for all liquids. In the same way when this bulging of the bottom of the drop is noticed, the amount of which is apparently also proportional to the surface tension, the falling drop must be heavier than it should be for that diameter, judged by the results obtained from a tip which exhibits no bulging; for here the weight falling would not simply be proportional to the diameter (or area) of the tip, which remains constant, but also to the extent of the bulging, which varies with the nature of the liquid. In both cases it is probable that the weight of the drop, in place of being simply proportional to the surface tension, is proportional to it in a more complex way. It is clear here, at any rate, that the results found on a tip upon which the drop bulges cannot be compared with those found on a tip which produces a normal drop; and further, that on such a tip two liquids cannot be compared, unless, of course, they both bulge to the same extent.

A second thing noticeable in obtaining the above results is the effect of a tip which is too large, *i. e.*, one on which it is impossible to perfectly control the speed of formation of the drop just at the moment of its fall. Naturally, this is to a certain extent a question of the apparatus used, for it is quite evident that when a liquid is passing through but a few centimeters of capillary tubing the perfect control will be lost at a smaller diameter of tip than it would when the liquid passes through a length of several meters of the same tubing, for the viscosity of the liquid would then prevent absolutely and automatically any considerable speed of formation. It would be expected, then, that the largest tip which could be employed on the Morgan drop weight apparatus would be smaller

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than that which could be used successfully on such a form as that of Morgan and Higgins.[1]

The effect of the so-called lack of control, as far as it refers to a tip which is just too large, is apparently to change what has been practically a static phenomenon into one that is dynamic, resulting in the carrying down of an excessive amount of liquid due to spurting at the final moment of fall. Increase in the diameter of the tip, after perfect control is lost, however, apparently also has the effect of changing the profile of the drop, causing the sides of the drop, which are parallel or nearly so, when the control is perfect, to converge at the bottom, forming an inverted cone quite different in shape from the bag-like form produced under ideal conditions. This, naturally, would cause the drop to break at a different place, and cause the fall of a weight which is not comparable to that falling from a tip giving the normal shape of drop. It would seem, then, from these qualitative observations, that *the drops of various liquids falling from a tip are only to be compared when the drop profiles are similar; and the drop falls of its own weight alone.* It is quite evident, thus, that the important factors as to the tip upon which a liquid will give satisfactory results, are the volume of the drop and its surface tension; for the shape assumed by the drop is dependent not only upon its volume, but also upon the surface forces which would tend to condition the form assumed by this volume. It was for this reason that the above liquids were chosen for the work; for carbon tetrachloride, with its small surface tension and large density, gives, with one or two rare exceptions the smallest possible drop volume, accompanied by small surface tension; ether, with its small surface tension, and also small density, and consequently larger volume, the next larger; then benzene and pyridine, and, finally, quinoline, which with the exception of water and a few other liquids, gives the largest possible drop volume, with large surface tension.

The bulging effect was very noticeable on the 3.05 mm. tip in the cases of benzene, ether, pyridine, and quinoline, but was not so apparent on the two next larger. Carbon tetrachloride also bulged on the 3.05 tip, but its variation on the next two was not so striking. Benzene, ether, and pyridine seemed to bulge on the three smallest tips to practically the same extent, and thus should be comparable in a way on each tip.

On the tips from 4.51 to 5.50 mm. inclusive, the behavior of ether, benzene, pyridine and quinoline seems to be perfect, no bulging being noticeable, and the drop profile being the same in general, while perfect

[1] Much of the difficulty experienced by Morgan and Thomssen with beveled tips, and also with the first sharp-edged ones, it is thought now was due to the use of capillary tubing of too large a bore. This not only gave trouble, owing to the threads of liquid which could not be drawn back in the tube, but also introduced difficulty in control.

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control is still possible. The control of carbon tetrachloride seemed poor on the 4.69 mm. tip, and continued to get worse and worse, as the diameter of the tip increased, the drop becoming more and more abnormal in shape. With this liquid no special precautions were taken as to control, so that the results given can be corroborated by any one—this will explain any apparent difference in the above results and those obtained, only after much practice, by Morgan and Thomssen. The control of ether is lost before that of benzene, and that of pyridine before that of quinoline, which was satisfactory certainly on all tips up to that of 7.39 mm.

In order to show the effect of too small, as well as of too large a tip, the drop weight in milligrams has been divided in each case by the diameter of the tip in question; these values are given in Table II. It is to be remembered here that unfortunately the error in measuring the diameter is not the same in all cases, some tips being sharper as to edge, and more perfectly circular in section than others. This would account for small variations in the value.

TABLE II.

Values of $\frac{\text{drop weight in mg.}}{\text{diameter in mm.}}$.

Diameter.	Benzene.	Quinoline.	Pyridine.	Ether.	Carbon tetrachloride.
3.05	5.703	9.201	7.442	3.227	5.087
3.93	5.487	8.797	7.207	3.126	5.004
4.00	5.484	8.791	7.203	3.124	5.000
4.51	5.381	8.534	7.044	3.063	4.975
4.70	5.371	.....	.....	.....	5.006
4.98	5.372	8.530	7.056	3.061	5.033
5.31	5.372	.....	.....	.....	5.086
5.50	5.369	8.530	7.048	3.059	5.144
5.50[1]	5.370	8.531	7.049	3.059	.....
5.69	5.366	8.531	7.043	3.076	5.194
5.85	5.359	8.494	7.042	3.078	5.248
6.20	5.369	8.497	.....	.....	5.263
6.55	5.397	8.504	7.045	3.154	5.293
6.84	5.432	8.496	7.047	3.178	5.354
7.39	5.510	8.547	7.084	3.249	.....
7.86	5.576	8.605	7.135	3.320	.....

The numbers in heavy type here indicate the tips which should give comparable results by any treatment. It will be noted that in general the values are too large for the smaller tips, then remain constant with an increase in the diameter, and then increase again; exactly as was forecasted from the qualitative observations. For carbon tetrachloride, apparently, but few tips could be used which would lead to identical

[1] Tip used by Morgan and Thomssen. The other though of the same diameter had no flaws, and the edges were sharper.

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results (without very special precautions as to control), *viz.*: those which are just smaller or just larger than 4.5 millimeters in diameter. There are but few liquids, however, which could give as much difficulty as this, for it is due to a very small drop volume, accompanied by very small surface tension; one example of this, perhaps the only one, is nickel carbonyl. *It will be observed that on the 4.51 mm. tip we could expect to obtain comparable results for all liquids, for even quinoline with its large drop volume shows no bulging upon it. We may conclude from Table II, then that Tate's other law—that the weight of a drop falling from any tip is proportional to the diameter of the tip—holds rigidly between certain definit limits, for all the liquids examined—and the only reason that it does not hold for all liquids on all tips is that the bulging of the drop on the smaller tips, and the opposite change of profile on the larger ones, causes the drop which forms and falls to obey laws which are not general, but which hold only for related liquids, i. e., for those with which the bulging, or change of shape in the opposite direction, would have the same weight-increasing effect.*

For *benzene*, using the values of w/r which are in heavy type, we find the relationship between drop weight and diameter; in other words, the analytical expression of Tate's first law, to be

$$w = 5.37 \times 2r, \quad \text{or}$$
$$w = 1.709 \times 2\pi r,$$

where w is in milligrams, $2r$ lies between 4.51 and 6.20 millimeters, and the temperature is 27.8°.

How well this expression of Tate's law holds for benzene; *i. e.*, how well the values of w thus calculated agree with those directly observed is shown in Table III.

TABLE III.

w FOR BENZENE CALCULATED FROM $w = 5.37 \times 2r$ AT 27.8°.

Diameter.	Wt. 1 drop calc.	Wt. 1 drop obs.	Δ.
4.51	24.219	24.269	0.050
4.70	25.239	25.245	0.006
4.98	26.743	26.753	0.010
5.31	28.515	28.526	0.011
5.50	29.535	29.530	0.005
5.69	30.555	30.532	0.023
5.85	31.415	31.349	0.066
6.20	33.294	33.287	0.007

A glance at the column of differences here shows the worst disagreement between the calculated and the observed values of drop weight to be about 0.2 per cent. Since the measurement of diameter can be considered accurate to only about 0.01 mm., however (*i. e.*, to 0.25 per cent. on the 4.51 mm. tip, and 0.17 per cent. on the 5.85 one), this agreement is as close as could possibly be hoped for.

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To show that the same kind of a relationship between drop weight and diameter of tip holds also for each of the other liquids; and further, to show the relationship existing between the weights of different liquids falling from the same tip, the indirect method already used in the previous papers is best employed; *i. e.*, that based upon the Ramsay and Shields form of equation

$$w\left(\frac{M}{d}\right)^{2/3} = k(t_c - t - 6).$$

It is quite evident here that in comparing different tips with the same liquid, that the w values must be related to one another as are the k values found for benzene on the two tips. For example, for benzene, we would have, at the same temperature of observation, t,

$$w'\left(\frac{M}{d}\right)^{2/3} = k'_B\ (288.5 - t - 6),$$

and

$$w''\left(\frac{M}{d}\right)^{2/3} = k''_B\ (288.5 - t - 6).$$

i. e., $w' : w'' : : k'_B : k'_B : .$ For different liquids on the same tip, then, using the value of t_c as given in the previous papers, and calculated for any one tip from its k_B value, *viz.*: 521.3° for quinoline, 346.6° for pyridine, 195° for ether, and 283.2° for carbon tetrachloride, constants, k, should be calculated for each liquid, *if the w values are properly related*, which are the same as the k_B value for that tip. In this way we can find the limits of diameter between which the drop weight method can be used for the purposes already discussed in the previous papers. Naturally, we would expect here only to get satisfactory results for those tips which in Table II gave uniform values for the $w/2r$; but the comparison is somewhat more satisfactory than that, owing to the fact that here there is no term of doubtful accuracy; the drop weight, and consequently the k value, can be determined in general with a much smaller percentage error than is found in the measurement of diameter, even under ideal conditions.

In Table IV are given the values of k for each of the liquids, using the values of t_c given above. In this table only those tips are considered which give satisfactory results as to the value of k, the diameters, as will be observed, being those already fixed by the ratio $w/2r$.

TABLE IV.—k VALUES NECESSARY TO GIVE ABOVE VALUES OF t_c.

	Diameter of tip, mm.						
Liquid	*4.51*	*4.70*	*4.98*	*5.31*	*5.50*	*5.50*	*5.69*
Benzene	1.908	1.985	2.103	2.243	2.322	2.321	2.400
Quinoline	1.906	.....	2.104	.....	2.324	2.323	2.404
Pyridine	1.906	.....	2.105	.....	2.323	2.323	2.401
Ether	1.909	.....	2.107	.....	2.326	2.325	[2.419]
Carbon tetrachloride	1.908	[2.000]	[2.131]	.....	.....	.....	.....
Average	1.907	.....	2.105	.....	2.324	2.323	2.402

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It will be noted here that a tip of the diameter of 4.51 millimeters leads to satisfactory results with all liquids, from carbon tetrachloride, with its minimum drop volume and very small surface tension, to quinoline with its very large drop volume and large surface tension. In other words, even a liquid such as quinoline, giving an exceedingly large drop volume, can be used on this tip without danger of the results being affected by a bulging of the drop.[1]

We are now in position to calculate the exact size of each of the tips used in the previous papers of this series, where only approximate values from a direct measurement with a micrometer were made. The values given are now found to have been throughout about 0.1 mm. too large. The tip used by Morgan and Thomssen, for example, from the relationship $k_{B-4.51} : k_{B.M\&T} :: 4.51 : 2r$ is found to be 5.50 millimeters, which also agrees with the recent, direct, measurement; by a similar proportion that of Morgan and Daghlian is found to be 5.64, and that of Morgan and Schwartz 5.53 millimeters.

It is also necessary here to see if by any chance a liquid already studied has suffered owing to a lack of control. As was mentioned in an earlier paper, ethylene dibromide is a liquid somewhat of the type of carbon tetrachloride, so that the results of Morgan and Thomssen on the 5.50 mm. tip may be slightly high. This would not, as has already been explained, affect the definition of the normal molecular weight, but the determination of the exact value of t_c, *i. e.*, that found on a tip on which the control is certainly perfect, where the value might be slightly different, must be left for future work. The only other liquid which could possibly be affected by more perfect control is bromine, which forms a drop of small volume but has sufficient surface tension to make the drop appear normal in profile, on the tip used by Morgan and Daghlian. If the control was not perfect here it was not noticeable to the eye, so that a smaller tip could only give a very slightly smaller result, if it changed it at all.

[1] *Water on this tip leads to a drop weight which is just what it should be, according to the relationship $w' : w'' :: k'_B : k''_B$, where w'' is the weight on a very much larger tip, k''_B being its k value for benzene. This shows that even water, forming as it does the largest known drop volume, also behaves normally on this small tip, and does not show any effect of a bulging of the drop. It would appear, then, that a tip of this diameter, 4.51 millimeters, is a universal tip on this apparatus, holding for all liquids. On larger ones, carbon tetrachloride, and perhaps a few others which are similar, would lead to results that are too large, owing to the lack of perfect control of the drop; but no other would probably fail to hold a smaller tip than 5.7 mm., on which the control of ether first becomes poor. In short, then, this 4.51 tip is not too small for the liquid giving the largest possible drop volume, nor is it probably too large for any known liquid at temperatures at which it would be likely to be used. Further, in case it were too large, the visible lack of control would warn the observer, and a smaller tip, the standard, benzene, value for which could be calculated from the above benzene values, and the measured diameter of the tip, assuming that benzene does not bulge, could be used.*

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The constants for the larger and smaller tips, which were not included in Table IV, are given in Table V. Here for each tip is also given the k value as calculated for benzene on the assumption that it always follows the law observed for the values given in Table IV.[1] These are the values which could be used as the standard, for example of a smaller tip, in the case that a liquid were used which gives such a small drop volume, if such there be, as to fail to give a good result on the 4.51 mm. tip. It will be noted from the Table that the relationship is just what was forecasted from Table II. As control is lost, the drop weight, and consequently the k value, becomes too large. Thus the control of benzene is lost before that of pyridine, which does not hold on as large a tip as quinoline, all of which is in perfect accord with the data in Table II.

TABLE V.—VALUES OF k NECESSARY TO GIVE ABOVE t_c VALUES.

	Diameter of tip, mm.								
Liquid.....	*3.05*	*3.93*	*4.00*	*5.85*	*6.20*	*6.55*	*6.84*	*7.39*	*7.86*
Calculated k. [$k = 0.4224 \times (2r)$]....	1.288	1.660	1.690	2.471	2.619	2.767	2.889	3.122	3.320
Benzene.....	1.364	1.695	1.724	2.465	2.617	2.779	2.921	3.303	3.446
Quinoline	1.390	1.712	1.741	2.461	2.609	2.758	2.878	3.126	3.350
Pyridine.....	1.360	1.697	1.726	2.469	.....	2.765	2.888	3.137	3.360
Ether.....	1.360	1.698	1.727	2.488	.....	2.855	3.005	3.318	3.607
Carbon tetrachloride....	1.319	1.672	1.701	2.589	2.752	2.925	3.089	.....	.....

The slightly low results for quinoline, as contrasted with the values calculated from the formula $k = 0.4224 \times 2r$ for benzene, on the 5.85, 6.20, 6.55 and 6.84 mm. tips, are probably due to a slight trace of water in the quinoline, for these tips were the last ones studied, and since the quinoline showed no trace of color, it was not redistilled before the determinations, and the calculations were not made until all was finished. The values for pyridine, on the other hand, appear to be in remarkable agreement with the calculated values on the 5.85, 6.55 and 6.84 mm. tips. The results for benzene and pyridine are always more to be relied upon than those for other liquids, for these when once obtained in the pure state undergo no change on standing, while the others must always be redistilled just before each determination. The pyridine, on all the larger tips, was determined here according to the procedure advocated in an earlier paper, *i. e.*, the remaining drop was always drawn back after each one fell, so that every drop was as normal as a first drop, and exhibited no trace of a pulling away from the edge of the tip, which is often noticed when successive drops are formed without this precaution. The only condition necessary in the determination of a liquid at a temperature as near the boiling point as 27.8° is to that of ether, is the assur-

[1] $k = 2r \times 0.4224$, r in millimeters.

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ance that the blank in every way duplicates exactly the conditions holding during the determination of the weight of the larger number of drops. In most of the cases above this liquid was also studied at 0°, to confirm the value at the higher temperature, with the result that a practically identical value of k was found at both temperatures.

Naturally, for the general drop weight method, the results in this table have little importance, for the tips lying in diameter between 4.51 and 5.50 mm. are the ones that would be used with it, and on them as has been shown already (Table IV), all liquids, with but a few exceptions, which can be recognized as such by the eye, as soon as the first drop forms and falls, give perfectly satisfactory results.

Since we find constant calculated values of k for the liquids on the tips with diameters between 4.51 and 5.50 mm., we would naturally expect to get a value of surface tension, from the proportion $\gamma : w : : K_B : k_B$, (where k_B is the drop weight constant for the tip, as found for benzene) which is constant for each liquid, independent of the size of the tip, so long as it is within the above limits. Using for K_B the value 2.1012, as found from the surface tension results of Ramsay and Shields, we obtain the values given in Table VI.

Combining the relationship

$$w = 5.37 \times 2r$$

or

$$w = 1.709 \times 2\pi r,$$

which we found for benzene with the above proportion, *viz.*:

$$k_B : K_B : : w : \gamma,$$

we find the relationship between drop weight, diameter, and surface tension for any liquid at 27.8° to be

$$w = 0.06397 \times (2r)\pi\gamma,$$

where γ is given in dynes per centimeter. The values of γ resulting from the application of this formula to the drop weight results of the various liquids are given in Table VII; these values, naturally, should differ from those in Table VI only by an amount equal to the error in the original equation for the variation in the drop weight of benzene with the diameter of the tip. Of course it is to be remembered here that the result

TABLE VI.—SURFACE TENSIONS IN DYNES PER CM. AT 27.8.°

$\gamma = w\ 2.1012/k_B$

Diameter of tip.	k_B.	Quinoline.	Pyridine.	Ether.	Carbon tetrachloride.
4.51	1.908	42.39	35.04	15.22	24.71
4.70	1.985	.....	.....	.....	.....
4.98	2.103	42.44	35.10	15.23	.....
5.31	2.243	.....	.....	.....	.....
5.50	2.322	42.47	35.09	15.23	.....
5.50	2.321	42.47	35.09	15.23	.....
5.69	2.400	42.49	35.08	[15.32]	.....
Average.....		42.45	35.08	15.23	24.71

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in VI could be obtained at any temperature at which w is known, while results from the equation used in VII could be found only from a drop weight at 27.8°.

TABLE VII.—SURFACE TENSIONS IN DYNES PER CM. AT 27.8°.

$$\gamma = w/0.063972 \times (2r)\pi.$$

Diameter of tip.	Benzene.	Quinoline.	Pyridine.	Ether.	Carbon tetrachloride.
4.51	26.75	42.42	35.06	15.23	24.73
4.70	26.75	.....	.....	.....	.....
4.98	26.74	42.46	35.12	15.24	.....
5.31	26.75	.....	.....	.....	.....
5.50	26.72	42.45	35.07	15.22	.....
5.50	26.71	42.44	35.06	15.21	.....
5.69	26.70	42.45	35.05	[15.31]	.....
Average.....	26.73	42.44	35.07	15.23	24.73

These values of surface tension are those which, with the Ramsay and Shields' constant 2.1012, will lead to the values already given of t_c, from which the k values were calculated. The values for benzene are the same as those which would have been found by Ramsay and Shields at this temperature; those for quinoline are practically the values that Bolle and Guye would have found, for their average value of the calculated t_c (see No. IV) is 522.4°, in place of the 521.3° we have used; the pyridine would agree very well with the value Dutoit and Friederich would have found, for their calculated t_c is 346.2° in place of our 346.6°; the value of carbon tetrachloride is that found by Ramsay and Shields, *i. e.*, leads to the same t_c as do their values at other temperatures, while the ether gives the same value as would be extrapolated from the higher temperature values of Ramsay and Shields.

The results of this research may be summarized as follows:

1. The drop weights of benzene, quinoline, pyridine, ether and carbon tetrachloride have been determined with the Morgan drop weight apparatus at 27.8°, on sixteen different, sharp, straight-edged tips, varying in diameter from 3.05 to 7.86 millimeters.

2. On the smaller tips the drop of liquid, instead of rising over the edge of the tip, as might be expected, was found to bulge at the bottom, extending there beyond the continuation of the sides of the tip, thus leading to high results; while on the larger tips, in addition to the loss of the perfect control of the drop, which is first observed, the profile of the drop is found to undergo a change which makes it appear quite different from the normal bag-like one, with its nearly parallel sides, for it converges at the bottom, which causes the drop to break away at a different point, and leads to results which are too high.

3. All liquids, from water, forming the largest possible drop volume, to carbon tetrachloride, which gives practically the smallest, are found

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to give perfectly satisfactory results from all points of view, on a tip with a diameter of 4.51 millimeters; while, excluding carbon tetrachloride, and possibly a few other similar liquids, characterized by a very small surface tension and a large density, which then form drops of minimum volume, equally satisfactory results are obtained on all tips with diameters between 4.51 and 5.50 mm.; and higher, for many liquids.

In other words, it is shown that when the drop profile is not abnormal to the eye, and the control of the drop is perfect, Tate's first law—the weight of a falling drop is proportional to the diameter of the tip from which it falls—holds rigidly.

4. Surface tensions in dynes, calculated from the benzene constants and the drop weight from the tip employed (*i. e.*, by aid of the proportion $\gamma : w : : K_B : k_B$) are found to agree on all tips from 4.51 to 5.50 mm., independent of the diameter of the tip, as long as the drop profile is normal and the control of the drop is perfect; in other words, for all liquids except carbon tetrachloride, which gives perfectly satisfactory results on tips around 4.5 mm. in diameter only, owing to its exceedingly small drop volume.

Surface tensions in dynes for these liquids are also calculated at 27.8° by aid of the formula $\gamma = w/0.06397 \times (2r)\pi$, which is also found to lead to results independent of the diameter, and which agree with the values calculated from the above proportion.

5. It is to be concluded from this investigation that the Morgan drop weight apparatus will give satisfactory results when the tip diameter lies between 4.51 and 5.50 millimeters, although if such a liquid as carbon tetrachloride is to be used it would be necessary to reduce the tip diameter to 4.51 mm., which will probably give satisfactory results for every known liquid.

LABORATORY OF PHYSICAL CHEMISTRY.

ANHYDROUS HYDRAZINE. I. A CONVENIENT APPARATUS FOR THE PREPARATION OF ANHYDROUS HYDRAZINE.

BY C. F. HALE AND FRED F. SNETTERLY.

Received May 26, 1911.

The first compound of hydrazine was prepared in 1875 by E. Fischer[1] by the reduction of a diazonium compound with potassium bisulfite. Curtius[2] obtained the sulfate of hydrazine by digesting an aqueous solution of triazoacetic acid with dilute sulfuric acid. By distilling hydrazine hydrate over barium oxide, Curtius and Schulz[3] attempted to prepare

[1] *Ber.*, 8, 589 (1875).
[2] *Ibid.*, 20, 1632 (1887); Curtius and Jay, *J. prakt. Chem.*, [2] 39, 27, 107 (1889).
[3] *J. prakt. Chem.*, [2] 42, 521–49 (1890).

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anhydrous hydrazine but obtained only a mixture of this substance with the hydrate.

Lobry de Bruyn succeeded in isolating hydrazine by either one of two methods: The first[1] of these methods consisted in heating hydrazine monochloride in absolute methyl alcohol with the calculated amount of sodium methoxide and repeatedly distilling the filtered liquid. The last fraction of the distillate, containing 82.6 per cent. of free hydrazine, was further concentrated by freezing out the hydrazine, with the result that a solution containing 92 per cent. of the compound was finally obtained. The second[2] consisted in the dehydration of hydrazine hydrate by means of barium oxide. Small quantities of the hydrate were added to an excess of barium oxide, the resulting mixture was heated to a temperature of from 110° to 120° for several hours in an atmosphere of hydrogen, and finally distilled under a pressure of from 100 to 150 mm. of mercury. The distillate contained from 96 to 97 per cent. of hydrazine. A second distillation over a comparatively small amount of fresh barium oxide yielded pure anhydrous hydrazine. An analysis of this product gave the results, 87.9 per cent. nitrogen and 12.5 per cent. hydrogen (theory, 87.5 per cent. nitrogen and 12.5 per cent. hydrogen).

Dschawachow[3] obtained free hydrazine by heating the dry hydrazine borate, $(N_2H_4)_2(B_2O_3)_6$, to a temperature above 260°.

Stollé and Hofmann[4] suggested the use of hydrazine carboxylic acid ($NH_2NHCOOH$) and of the hydrazine salt of this compound in the preparation of anhydrous hydrazine and recommended the distillation of these compounds over calcium oxide or barium oxide.

Stähler[5] investigated the action of calcium oxide upon hydrazine hydrate and utilized this reaction in the preparation of anhydrous hydrazine. He also suggests the possible existence of either a solid solution of hydrazine in calcium oxide or hydroxide or a compound of the formula $Ca(ON_2H_5)_2$, which may be subsequently decomposed into calcium hydroxide and hydrazine.

Ebler and Krause,[6] in connection with their study of metallic hydrazides, prepared 99.7 per cent. hydrazine by distilling the hydrate twice over barium oxide and finally freezing out the pure hydrazine from the distillate.

Raschig[7] made use of sodium hydroxide in effecting the dehydration

[1] *Rec. trav. chim.*, 13, 433–40 (1894); see also *Ber.*, 28, 976 (1895), Ref.

[2] *Rec. trav. chim.*, 14, 858 (1895); 15, 174–84 (1896); see also *Ber.*, 29, 770 (1896), Ref.

[3] *J. russ. phys.-chem. Soc.*, 34, 227–30 (1902); *Chem. Zentr.*, 1902, I, 1393.

[4] *Ber.*, 37, 4523–4 (1904).

[5] *Ibid.*, 42, 3018–19 (1909).

[6] *Ibid.*, 43, 1690 (1910).

[7] *Ibid.*, 43, 1927 (1910).

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of hydrazine hydrate. A mixture of equal parts of the two substances was heated at a temperature of 113° for two hours and the hydrazine was then distilled over into a suitable receiver. Without submitting analytical details, the author states that an almost theoretical yield of absolutely anhydrous hydrazine was obtained.

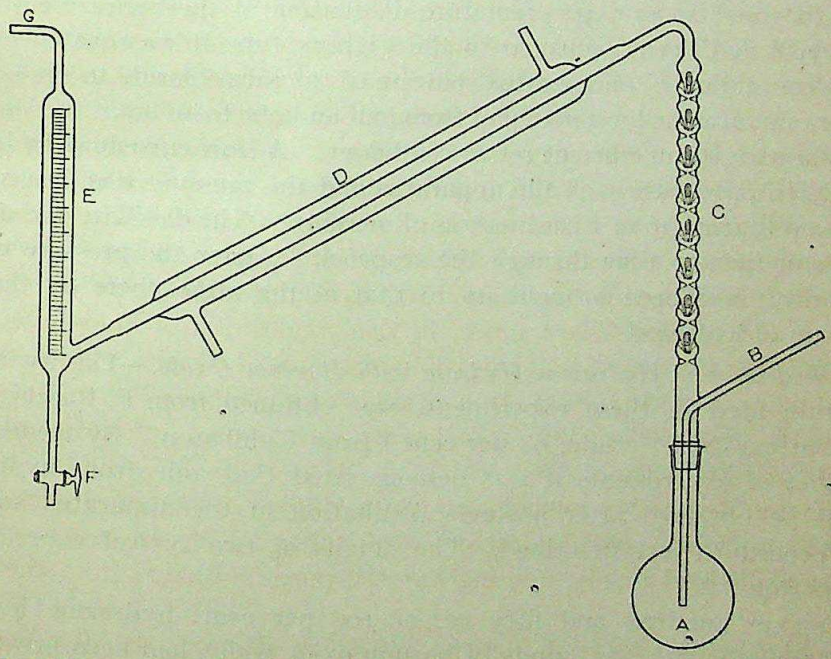
Stollé[1] obtained nearly anhydrous hydrazine by the action of sodium amide upon hydrazine hydrate in excess, which he found to proceed in the manner indicated by the equation

$$N_2H_4.H_2O + NaNH_2 = N_2H_4 + NH_3 + NaOH.$$

When the sodium amide was used in excess he found the reaction to proceed further in concordance with the equation[2]

$$N_2H_4 + NaNH_2 = NaN_2H_3 + NH_3.$$

In preparing the comparatively large amounts of anhydrous hydrazine that have from time to time been required for certain investigations in progress in this laboratory during the past three years, a special form of apparatus has been employed, in the designing of which, the following considerations have been borne in mind: (1) exclusion of all cork and



rubber stoppers and connections; (2) provision of a suitable distilling column; (3) provision for distillation in a current of hydrogen and under reduced pressure; and (4) provision of a suitable receiver for the measurement, fractionation, sampling, or storing of the distillate.

[1] *J. prakt. Chem.*, [2] 83, 200 (1911).

[2] See also Scandola, *Boll. soc. med.-chir. Pavia*, 1910; *Chem. Zentr.*, 1910, II, 544, and Ebler and Krause, *loc. cit.*

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Description of Apparatus.—After a series of preliminary experiments, the form of apparatus shown in the subjoined sketch was adopted. The 500 cc. flask *A* is connected by means of a ground glass joint with the Vigreux[1] distillation tube *C*. The tube *B*, which serves as an inlet for hydrogen, is fused into the wall of *C* and extends somewhat below the middle of the flask *A*. The distillation tube is fused to an ordinary Liebig condenser *D*, which in turn communicates with the graduated receiver *E*. The tube *G* is connected with a convenient form of vacuum pump provided with a suitable accessory reservoir and absorption tubes, and with a mercury manometer.

General Procedure.—Measured amounts of the hydrazine hydrate and the solid dehydrating agent in excess were brought together in the flask *A* under such conditions as to prevent the loss of hydrazine vapor by too rapid heating of the mixture. This was satisfactorily accomplished either by slowly adding small pieces of the solid to the entire mass of the liquid, or by pouring the hydrate a little at a time upon the solid. In either case, it was found advisable to immerse the flask, from time to time, in cold water to prevent premature distillation of the hydrazine. After the flask had been connected to the Vigreux tube it was heated over a bath containing a concentrated solution of calcium chloride to the boiling point of hydrazine for a period of from half an hour to an hour, the Vigreux tube serving as an efficient reflux condenser. A slow current of hydrogen was then passed through the apparatus and the pressure was, in general, reduced to from 30 to 2 centimeters of mercury. The distillate was drawn off from time to time through the stopcock *F*, after the pressure in the apparatus had been brought up to that of the atmosphere by the admission of hydrogen.

Dehydration of Hydrazine Hydrate with Barium Oxide.—The hydrazine hydrate used in these experiments was obtained from F. Raschig, and the barium oxide (crude, 98 per cent.) from Kahlbaum. By means of a number of experiments it was demonstrated that anhydrous hydrazine could be obtained after a single distillation in the apparatus and by the procedure just described. The details of two typical experiments are as follows:

(1) One hundred and fifty cc. of 100 per cent. hydrazine hydrate were treated with 415 grams of barium oxide which had been previously crushed in a mortar. The entire distillate obtained weighed about 92 grams and was shown by subsequent analysis by the method of Rimini[2] to contain 99.83 per cent. of hydrazine. These figures correspond to a yield of approximately 92.5 per cent. of the theory.

[1] *Bull. soc. chim.*, [4] 3, 855 (1908).

[2] *Gazz. chim. ital.*, 29, I, 265–9 (1899); *Atti accad. Lincei Roma*, [5] 15, II, 320; *Chem. Zentr.*, 1906, II, 1662.

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(2) One hundred cc. of 93.6 per cent. hydrazine hydrate and 530 grams of crushed barium oxide were used in this experiment. The distillate contained 99.9 per cent. of hydrazine and weighed 59.5 grams, which corresponds to a yield of about 96.5 per cent. It is to be noted that a considerable excess of barium oxide above the amount theoretically required for pure hydrate was used in this experiment since the hydrazine hydrate used was not of a high degree of purity. In case 100 per cent. hydrazine hydrate is used, however, an amount slightly in excess of the theoretical quantity of barium oxide will suffice.

Dehydration of Hydrazine Hydrate with Barium Hydroxide.—In connection with the investigation of the interaction of barium oxide and hydrazine hydrate, it may be of interest to record the behavior of barium hydroxide toward hydrazine hydrate. Since, in the experiments, the same apparatus was employed, the results obtained are comparable with those obtained with barium oxide. The barium hydroxide used was shown, by analysis, to contain 80.23 per cent. barium (theory for Ba in $Ba(OH)_2$, 80.16 per cent.). In one experiment a mixture of 97 per cent. hydrazine hydrate and barium hydroxide yielded, on distillation, a product containing 78 per cent. hydrazine (theory for hydrazine in hydrazine hydrate, 64 per cent.). A second distillation over the same material gave a distillate containing 88 per cent. of hydrazine.

In another experiment, 51.5 grams of 78 per cent. hydrazine mixed with 40 grams of 88 per cent. hydrazine were treated with 400 grams of barium hydroxide and were subjected to distillation. The distillate, containing 93.1 per cent. hydrazine, was redistilled over 200 grams of new barium hydroxide with the result that the first fraction contained 96 per cent., and the second 93.5 per cent. of hydrazine. From these results it is apparent that barium hydroxide is, as was to be expected, a much less efficient dehydrating agent than barium oxide.

Dehydration of Hydrazine Hydrate with Sodium Hydroxide.—In order to compare the new method for the preparation of anhydrous hydrazine suggested by Raschig[1] with the older method of de Bruyn, Mr. T. W. B. Welsh, of this laboratory, has subjected 100 per cent. hydrazine hydrate (Raschig) to the action of sodium hydroxide in the apparatus described in a preceding paragraph.

Experiment 1.—Two hundred and fifty grams of hydrazine hydrate were heated to the boiling temperature for two hours with 250 grams of ordinary sodium hydroxide. The mixture was then distilled, and the distillate was caught in four fractions, which weighed 55, 54, 55 and 10 grams, respectively, and which were found to contain 98.6, 97.5, 95.0 and 87.0 per cent. of hydrazine.

Experiment 2.—Two hundred and fifty grams of hydrazine hydrate were heated as before with an equal weight of fused sodium hydroxide. The first three of the six fractions into which the distillate was divided weighed 25, 23 and 21 grams, and contained 99.3, 98.1 and 98.1 per cent. of hydrazine.

[1] *Loc. cit.*

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Fractional Distillation of Hydrazine Hydrate.—As a blank experiment, it was deemed advisable to study the fractional distillation of hydrazine hydrate in the absence of dehydrating agents, in the same apparatus and under conditions similar to those governing the preceding experiments. It has been shown by Scott[1] "that at 100° in a vacuum hydrazine hydrate in vapor is dissociated into hydrazine and water to the extent of 58 per cent., and that at 140° this dissociation is complete." From these facts it is, of course, to be expected that the first fractions obtained by distilling hydrazine hydrate should contain less, and that the middle fractions should contain more than 64.0 per cent., of hydrazine (theory for N_2H_4 in $N_2H_4.H_2O$ = 64.0 per cent.). The results obtained by Mr. Welsh were as follows:

Experiment 1.—Two hundred and fifty grams of hydrazine hydrate (Raschig, 100%) were distilled, in a slow, steady current of hydrogen, in the apparatus already described. The first six 25 cc. fractions were found to contain the following respective percentages of hydrazine: (1) 56.87, (2) 61.50, (3) 62.23, (4) 63.43, (5) 65.03, (6) 65.22.

Experiment 2.—The preceding experiment was duplicated, and the distillate was divided into 10 fractions, the first 9 containing about 25 cc. each, and the tenth somewhat less. Analysis showed the percentages of hydrazine to be respectively as follows: (1) 56.64, (2) 60.19, (3) 61.77, (4) 62.97, (5) 64.36, (6) 65.62, (7) 72.27, (8) 67.22, (9) 68.05, (10) 68.82.

Summary.

In the foregoing paragraphs has been described a convenient form of glass apparatus for the preparation of anhydrous hydrazine by the action of any suitable dehydrating agent upon hydrazine hydrate. The action upon hydrazine hydrate (1) of barium oxide, according to the method of de Bruyn, (2) of barium hydroxide, and (3) of sodium hydroxide, according to the procedure of Raschig, has been studied under comparable conditions. As a blank experiment, pure hydrazine hydrate has been subjected to fractional distillation in the same apparatus and under conditions similar to those prevailing in the other experiments.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

THE STEARATE SEPARATION OF THE RARE EARTHS.

BY C. W. STODDART AND C. W. HILL.[2]

Received April 22, 1911.

Introduction.—One of the principles of separating the rare earths by

[1] *J. Chem. Soc.*, 85, 913–8 (1904).

[2] The investigations covered by these papers were undertaken at the suggestion of Professor Victor Lenher whom the authors wish to thank for his advice and encouragement. They were originally presented as theses for the doctor's degree by their respective authors.

Thanks are also due Mr. H. S. Miner, of the Welsbach Company, for the material employed.

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fractional precipitation depends on the slight differences in basicity of the earths. Any reagent which forms insoluble compounds with the earths may be used; but if the reagent in question has weak acidic or basic properties, it is of distinct advantage. When, for example, a salt of a strong base and a weak acid is added in dilute solution to a mixture of the rare earth nitrates, the strong base tends to unite first with the nitric acid radical of the weakly basic earths, since the salt of the weak acid is readily decomposed in the presence of the stronger acid. The rare earth metal is then free to unite with the weak acid to form an insoluble compound. As the fractionation proceeds the more strongly basic earths react, and as a result a much better separation is effected than in the case of a precipitant of stronger basic character.

Stearic acid is a weak organic acid of the fatty series, is of high molecular weight, and forms easily handled precipitates with the rare earths. It was therefore chosen as a reagent for attempting the fractionation of these difficultly separated elements.

Method of Fractionation.—The fractionation of rare earth mixtures as stearates was accomplished by the addition of an alcoholic solution of potassium stearate to a neutral solution of the earth nitrates, in quantity sufficient for the precipitation of only a fractional portion of the earths present.

The oxides of the earths were dissolved in nitric acid, the excess of acid removed by evaporation, and the syrupy residue taken up with water. It was found that if the stearate was added rapidly the precipitate was hard and lumpy, due to complete local precipitation where a large quantity of stearate came suddenly in contact with the earth nitrate. If, however, the stearate was added drop by drop, and the solution vigorously stirred, the precipitate was loose, fine-grained, easily washed, and the separation was excellent. Consequently the method finally adopted was to add, drop by drop, a hot alcoholic solution of potassium stearate to a cold, dilute, neutral solution of the earth nitrates. The mixture was agitated by a glass stirrer driven at high speed by a small electric motor. The stirring was continued several hours after the addition of the precipitant.

By using a Buchner funnel with two thicknesses of filter paper, it was possible to wash the precipitate rapidly. The filtrate was evaporated to the original volume and cooled before the addition of the next portion of stearate. The washed precipitate was ignited for atomic weight determination. (NOTE.—When fractions are to be combined without determination of the atomic weight, as in the case of large amounts of materials and several similar series, the precipitated stearates suspended in water may be decomposed by nitric acid. The free stearic

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acid can be removed mechanically, and the resulting nitrate solution combined with others. This permits of very rapid fractionation.)

The first fraction of a series was always smaller than the others, and the precipitate had a tendency to be hard and lumpy, notwithstanding the care used in adding the precipitant slowly. This was due to the liberation of free stearic acid by the slight excess of nitric acid often remaining in the earth solution. It was found advizable, therefore, when the solution was acid, to add a small amount of stearate and remove the free stearic acid before proceeding with the separation.

The use of a mechanical stirrer changed the nature of the precipitate from a coarse, curdy texture to a fine, light material. Time is another factor entering into the more complete separation of the rare earths. If the mixture of precipitate and solution is stirred for a considerable length of time, a secondary decomposition takes place which materially changes the chemical composition of the precipitate. This fact is shown by the two experiments conducted as follows:

Seven-tenths of a gram of an oxide, the elements of which had an average atomic weight of 109.6, were dissolved in nitric acid, the solution evaporated, and the residue diluted with water to two liters. To this was added the thoroughly washed precipitate of earth stearates which had an average atomic weight of 97.4. This mixture was stirred for about twelve hours. At the end of this time the precipitate had changed physically from a coarse, curdy mass to a very fine-grained, light, fluffy material. The precipitate was removed, washed thoroughly, and the average atomic weight of the elements found to be 102.8. This increase in atomic weight from 97.4 to 102.8 showed that a very decided secondary decomposition had taken place between the solid stearate and the nitrate solution.

In another instance a mixture which indicated an atomic weight of 126 yielded a first fraction, the earth element of which had an atomic weight of 127.1. The atomic weight of the element of the same fraction stirred for forty-eight hours was changed to 135.2.

Preparation of the Stearate Solution.—Pure stearic acid which had a melting point of 69°–70° was used for the first fractionations. Later it was found that commercial stearic acid with a melting point of 55° was satisfactory. This material was approximately 50 per cent. stearic acid and 50 per cent. palmitic and oleic acids. Since the commercial acid is very much cheaper, and at the same time just as effective, its use is of great advantage.

The potassium stearate solution was prepared by dissolving stearic acid in 95 per cent. alcohol, neutralizing with a solution of potassium hydroxide, using phenolphthalein as indicator, and diluting with water to make a 50 per cent. solution. One cubic centimeter of the solution contained about two-tenths of a gram of stearic acid.

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Determinations of Atomic Weight and Absorption Spectra.—The atomic weight determinations were made by the Gibbs method of analyzing the oxalates, which was sufficiently accurate for this work.

Absorption spectra of 10 per cent. nitrate solutions through layers of solution 17.5 mm. thick were obtained by means of a Steinheil grating spectroscope. Comparisons were made with samples of rare earth salts prepared by Waldron Shapleigh and Eugene Demarçay.

Experimental Note.—It was observed during the washing of the precipitated stearates that the material tended to separate in the long cylinder employed, part of the precipitate floating on the surface and part of it sinking to the bottom. This suggested the possibility of a separation based upon the differences in specific gravity of the stearates of the various earths present. A mixture of yttrium earths with didymium and erbium earths was converted into nitrates and carefully precipitated as stearates. The precipitate was washed, suspended in water, and agitated continuously for a week by means of the rapidly revolving mechanical stirrer. It was then placed in an alcohol-water solution of a specific gravity which allowed the stearates to settle to the bottom. Water was added until three fractions had been obtained. Sodium chloride solution was added to separate the fourth and fifth fractions. The specific gravities (by hydrometer) of the solutions from which the fractions were removed and the atomic weights of the earth elements are tabulated below.

	Atomic weight.	Sp. gr. of solution.
Mixture	120.3	.....
Fraction 1 (small)	121.6	0.900
Fraction 2	120.8	0.950
Fraction 3	120.6	0.951
Fraction 4	120.8	1.040
Fraction 5 (remaining)	120.1	.....

There is evidence of a slight separation, especially with the first fraction which was small. The separation is not good in comparison with that obtained by other methods applied to the same mixture of earths, although it might be more striking with other mixtures. Opportunity has not been afforded the writers to repeat the experiment, nor to employ other mixtures of the rare earths.

I. THE STEARATE SEPARATION OF THE YTTRIUM GROUP (BY C. W. STODDART).

Yttrium Earths from Monazite.

Preparation of Oxides.—The material employed was in the form of oxalate from monazite, which was ignited, converted into nitrates, and the yttrium earths separated from the cerium earths by precipitating the latter as the double potassium sulfate in a saturated solution of potassium sulfate. The cerium earths were in such excess that a considerable quantity of yttrium earths was carried down with them either by inclusion or adsorption, although the presence of an excess of nitric acid prevented this adsorption to a very considerable extent. By treating the cerium earth double sulfate with additional water it was found possible to recover a further portion of the yttrium earths.

In this way several lots were obtained, amounting in all to six per cent.

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of the original roasted oxalates. The atomic weights of the different lots varied from 117.4 to 132.2, the latter containing some didymium. It was possible to tell with considerable accuracy when the characteristic absorption bands of didymium had disappeared, by using a hand spectroscope on an eight-inch layer of the filtrate from the cerium earth double sulfates.

Separations Effected.—The first fractionation was made on 10 grams of yttrium earth oxide with an atomic weight of 118.1. Nineteen fractions were removed by adding various amounts of an aqueous solution of potassium stearate. Table I gives the atomic weights of the fractions.

TABLE I.—ATOMIC WEIGHTS OF THE FIRST SERIES OF FRACTIONS.

Number of fraction.	Atomic weight.	Number of fraction.	Atomic weight.
1	124.5	11	120.7
2	127.0	12	123.1
3	129.2	13	121.6
4	119.7	14	118.9
5	125.4	15	118.9
6	125.3	16	113.3
7	123.3	17	107.9
8	123.3	18	102.7
9	124.4	19	103.7
10	120.5	..	...

The atomic weights do not diminish regularly from first to last, due in great measure to the changes in methods of fractionation. The precipitate in many instances was not homogeneous, owing to complete local precipitation having taken place where the precipitant was added too rapidly. Apparently such a large number of fractions is unnecessary, but the fact is clearly brought out that the stearate method is able to separate the rare earth oxides of atomic weight 118.1 into fractions varying from 129.2 to 102.7.

The second fractionation was carried out on 10 grams of earth oxide with an atomic weight of 117.4, using a solution of potassium stearate in 95 per cent. alcohol, and adding it drop by drop from a burette, it being necessary to warm the burette from time to time to keep the solution liquid. After the addition of the precipitant the mixture was shaken violently in a flask. Six fractions were removed, the atomic weight of each being as follows: 122.8, 119.8, 116.8, 115.6, 106.7, 103.7. From these results it is to be noted that approximately the same degree of separation may be effected in six fractions as in nineteen, if the conditions are slightly changed.

In order to try the method on a larger scale, 50 grams of rare earth oxides of atomic weight 118.1 were dissolved in nitric acid and fractionated with alcoholic potassium stearate. Each part of the first series was fractionated again and suitable fractions combined. In this way six-

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teen fractions were obtained and united according to their atomic weights into four portions, the atomic weights of each being 123, 120, 114, and 112.

The separation effected here was not particularly good. Sufficient time had not been allowed for equilibrium to be established. The precipitate was in many cases so coarse that some of the solution was occluded. Consequently, it was at this point that the method of fractionation was changed to the use of the mechanical stirrer and a solution of potassium stearate in 50 per cent. alcohol. Moreover, it was found that instead of obtaining fractions of equal weight, if several small fractions were first removed, the heavier earths could be separated more rapidly and a large fraction left, with materially lighter atomic weight. For example, with ten grams of oxide there were removed four fractions of 1.5 grams each, and one fraction of 4 grams.

With these improvements in method, the four portions mentioned above, having atomic weights of 123, 120, 114, and 112, were separated into numerous fractions, the various fractions in the different groups united according to the color of the ignited stearates and refractionated. The colors varied from dark brown to light buff. Thirty-three fractions were thus obtained. Three were united whose color was almost white and whose atomic weight was 92. This lot was separated into four fractions, the last one having an atomic weight of 90.6, and was practically pure yttrium. The quantity, however, was so small that further fractionation was impossible, although there is no doubt that yttrium of atomic weight 89 could have been obtained very easily from this material.

Absorption Spectra.—Twenty-nine of the thirty-three fractions in the last series were examined for absorption bands. Table II gives the wave

TABLE II.—ABSORPTION SPECTRA OF THE FIRST STEARATE FRACTION, OF THE TWENTY-NINTH STEARATE FRACTION, AND OF ERBIUM NITRATE (SHAPLEIGH'S).

First fraction.		Twenty-ninth fraction.		Erbium nitrate.	
		444.2	very faint		
				452.0	very faint
458.0 463.7	fairly strong	462.3	very faint	457.4 464.1	fairly strong very faint
493.7 496.4	very faint fairly strong	495.1	very faint	493.5 496.8	very faint fairly strong
529.1 435.7	very faint strong	529.4 532.6	haze fairly strong	527.6 533.0	very faint strong.
544.7	fairly strong	545.3	faint	545.6	faint
				550.5	very faint
580.2 589.9	faint	579.2 590.9	faint	579.5 590.2	fairly strong
647.5 651.1	fairly strong	648.4	faint	649.3	faint
				657.3	very faint
661.7	fairly strong	664.3	very faint	661.7	faint

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lengths for the first fraction and for the twenty-ninth fraction whose atomic weight was 101.4. In comparison there is given the spectrum of a sample of erbium nitrate prepared from monazite by Dr. Waldron Shapleigh.

Examining the table it may be seen that most of the lines are those of erbium, or at least of earths very closely associated with erbium, such as samarium, holmium, and europium. The lines fade markedly as the fractionation progresses, but persist throughout the series until there is obtained the last fraction which had an atomic weight of 90.6. This portion gave absolutely no absorption spectrum.

Yttrium Earths from Gadolinite.

To test the separation of the yttrium earths from gadolinite, about 8 grams of oxide, freed from the cerium group by precipitation of the latter with potassium sulfate, were separated into five fractions. The first fraction had an atomic weight of 109.6, the last fraction of 97.4. This material contained a higher percentage of yttrium than did the monazite earths, and the progress of the fractionation indicated a rapid approach to the separation of this element from its companions.

Behavior of Yttrium Earth Stearates towards Anhydrous Solvents.—In order to test the solubility of the stearates of the rare earths in anhydrous compounds and subsequently to investigate the ability of the latter to extract them differentially, a portion of the earth oxide of atomic weight 118.1 was dissolved in nitric acid, evaporated to a thick syrup, diluted with water, and all the rare earths precipitated by potassium stearate. The precipitate was filtered, washed, dried and pulverized.

A part of this substance was placed in a Schleicher and Schüll paper thimble in a Soxhlet extractor and subjected to extraction with *ether* for some time. Only stearic acid was removed. This was present in the original mass in the free state, having been liberated from the potassium salt by the excess of nitric acid in the original solution.

Benzene extracted a portion of the rate earths. A determination of the atomic weight of the extracted material gave 116.6, of the part remaining in the thimble, 117.5.

Carbon tetrachloride extracted a portion which gave an atomic weight of 116.9. The fraction remaining behind was 117.4 in atomic weight. Further treatment extracted practically all of the rare earth stearates.

Carbon disulfide extracted nothing but stearic acid.

Alcohol extracted only stearic acid.

Xylene extracted a portion whose atomic weight was 117.8. All of the material was soluble finally.

Toluene dissolved all of the material.

Chloroform extracted only stearic acid.

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Melted *naphthalene* and *anthracene* dissolved all of the material, as did hot *olive oil.*

From these results it can be seen that yttrium earth stearates are soluble in anhydrous compounds of relatively high boiling points, but there is no one rare earth stearate markedly different in solubility from the rest.

Discussion of Results.

In the year 1896, Drossbach[1] obtained by fractional precipitation with sodium hydroxide, and also by fractional crystallization of the sulfates, a white oxide whose element had an atomic weight of approximately 100. Also in 1896 Schützenberger and Boudouard,[2] by alternating the basic nitrate method with fractional crystallization of the sulfates, obtained a white oxide whose atomic weight was 102. Since these investigators were unable to decompose this fraction further, they assumed that they had an element whose atomic weight was approximately 100. In 1897 Urbain and Boudischovsky[3] by using the acetyl-acetonate method obtained several fractions whose atomic weights averaged about 100.

In 1900, however, Urbain[4] was able to carry the fractionation further with the ethyl-sulfate method, obtaining one portion whose atomic weight was 152, on one hand, and pure yttrium on the other. He claimed that the product obtained by Drossbach, Schützenberger and Boudouard, as well as by himself previously, was a mixture of pure yttrium and the terbium earths. In all the above cases the material employed was from monazite.

Referring back to the last fractions of the first two series by the stearate separation on page 1080, it will be noticed that the atomic weights were 103.7 in both cases. This may be the same fraction obtained by the investigators mentioned above. It is to be observed that this fraction of approximately 102 (average) is obtained only from monazite yttrium earths. In the stearate separation on the gadolinium earths no such fraction was obtained.

The earths of the yttrium group are characterized by such a similarity one with another, that by any method their separation is difficult. In the case of the yttrium earths from monazite, however, this difficulty of separation apparently reaches a climax when the mixture has an atomic weight of approximately 102. This particular fraction is so difficult of separation that, as seen above, some of the previous investigators went so far as to think that they had discovered a new element. The later work of Urbain, however, dispelled their illusion.

[1] *Ber.*, 29, 3, 2452.
[2] *C. r.*, 122, 697.
[3] *Ibid.*, 124, 618.
[4] *Ann. chim. phys.*, 19, 184.

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It is customary in preparing pure yttrium to use alternately various methods, since most reagents are unable to carry the separation beyond a certain point. A different reagent is necessary to effect a further separation. The fraction from monazite earths having an atomic weight of 102 presents more than ordinary difficulties of separation, even when the methods are changed. It is to be noted that the use of potassium stearate, however, as a means of separating these earths is in itself sufficient to carry the fractionation from the original material down to pure yttrium without using any other reagent. It is true that there is a momentary pause at the fraction of atomic weight 102, indicating a combination whose separation causes more than ordinary difficulty.

In explaining the cause of this difficulty in separating the fraction whose atomic weight is 102, two possibilities suggest themselves:

First, that there is a new element in monazite very closely allied with yttrium and so near like it in properties that it is very difficult to separate them. In passing, Crookes' victorium[1] might be mentioned. This element, which Crookes claims to have separated from samarskite, gadolinite, cerite, and other similar minerals, has an atomic weight of approximately 118, and is very like yttrium in properties. The presence of a new element, however, has been disproved by the work of Urbain, mentioned above.

Second, that there is formed a pseudo-compound of yttrium with other members of the group—a compound which gives an atomic weight of 102 for the element. The average atomic weight of the other members of the group is 166 and calculating with this average figure it would mean a compound of four parts yttrium to one part of the other members of the group.

Conclusions.

1. The stearate method is of distinct advantage over existing methods in many ways. The precipitate formed is easily filtered and washed, the precipitant cheap, the separations sharp and distinct. For the preparation of pure yttrium from monazite it is decidedly the best method known, and yttrium is one of the most difficult rare earths to separate pure. Only one reagent is necessary, and few fractionations are required, thereby saving a great amount of time, as well as of material, in a large number of manipulations. There is a brief pause in the progress of the fractionation at the portion which has an atomic weight of approximately 102.

2. The stearate method applied to the yttrium earths from gadolinite effects a rapid separation without the pause at the fraction having an atomic weight of 102.

3. Yttrium earth stearates are soluble in anhydrous compounds of

[1] *Chem. News*, **80**, 49.

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relatively high boiling point, but they are not extracted differentially by such solvents.

II. THE FRACTIONATION OF THE GADOLINIUM EARTHS AS STEARATES (BY C. W. HILL).

The experimental work here described was undertaken with the purpose of studying the adaptability of the stearate method to the fractionation of the gadolinium earths. The available material was Welsbach residues from monazite, and gadolinite. The treatments of the rare earths from the two sources are considered separately.

Separation of Rare Earths from Monazite.

The rare earths obtained from monazite as oxalates, ignited and converted into nitrates, were fractionally crystallized from the nitrate solution as the double magnesium nitrates, crystallization being continued until magnesium nitrate separated out. The crystallized part contained the major portion of the cerium, lanthanum, and the didymiums. From the remaining solution, three large fractions of insoluble double potassium sulfates were crystallized. The earths remaining in solution were treated as described on page 1087.

Insoluble Double Sulfate Portion. — The earths in the last insoluble double sulfate fraction were converted into hydroxides by boiling with sodium hydroxide. The hydroxides, after being washed, were dissolved in nitric acid, and the earths reprecipitated from the dilute nitrate solution by dilute ammonia, washed free from alkali and dissolved in formic acid.

Five large fractions of formates were obtained by the slow evaporation of the formate solution, and the earths remaining in solution were precipitated by ammonia. The earths in the large first formate fraction were converted into nitrates, hydroxides, and formates successively, and fractionated partly as formates (three fractions) and as hydroxides (last four fractions). The earths in the other formate fractions were precipitated fractionally with dilute ammonia. The atomic weights determined were:

SERIES I.

Formate fractions.	I.	II.	III.	IV.	V.	VI.
Subdivisions...	143.5	137	134	132	138.1	119.9
	...	...	...	...	132.4	...
	...	...	...	...	131.1	...
	...	...	...	...	...	...
	...	...	...	...	...	...
	135.1	...	...	...	...	...
	63.0	...	...	...	...	...

The last fraction of formate fraction I, showing an atomic weight of

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63, gave a white oxide, and its solution showed no absorption spectrum. It consisted of yttrium and scandium.

The fractions derived from the large formate fractions I and II were separated further by fractional precipitation of the stearates. Thirty-three fractions thus obtained were combined into six groups according to the color of the oxides and their relation to the other fractions, the more soluble of one group being combined with the less soluble portion of the group following (Series II).

The six groups were fractionated further as stearates into twenty-eight fractions, the atomic weights being as follows:

SERIES III.

138.0	146.9	144.7	150.8	144.8	146.5
...	...	...	...	...	...
...	...	...	...	...	...
...	...	...	147.5	...	...
...	128.9	131.6	...	...	...
...	...	...	...	124.6	...
113.6	...	...	...	...	...

In the first part of the work the atomic weights of only the extreme fractions were determined. This course is not advizable, since the first fraction of a group is usually lower in atomic weight than the second, and often approximates an average of the group. It is to be expected, with the earths under consideration, that the didymiums will be present to a greater extent in the first fractions of a series and that the atomic weight of some intermediate fraction will be greatest. The atomic weights in many of the tables confirm this statement. It is therefore necessary in accurate work to determine the atomic weights of practically all the fractions of a series.

The fractions last described were combined according to their atomic weights into eight groups, the atomic weights of which approximated 148, 145, 142, 140, 137, 132, 128, 124. The first three groups after removal of the cerium by hydrogen peroxide and ammonia were taken for further separation as stearates. The atomic weights of the different groups and fractions are given. Each group was obtained by combination of fractions of the preceding group which had nearly the same atomic weight.

	SERIES IV.			SERIES V.		
At. wt. of group.....	(148)	(145)	(142)	(146)	(144)	(140)
At. wt. of fractions..	145.8	146	148.4	146.2	148	144
	...	...	...	147.5	139.9	143.3
	...	...	...	147.4	...	143.2
	...	121.6	...	...	...	142.1
	131.3	...	137.6	120.1	...	141.3
				118.9	...	...
				...	...	126

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	Series VI.			Series VII.		
At. wt. of group....	(147.6)	(143)	(144)	(153.1)	(146.6)	(143.4)
At. wt. of fractions	153.1	150.4	145.3	152.3	151.2	149.8
	146.6	150.2	143.1	150.3	145.7	137.1
	142.9	143.4	140.9	147.8	...	...
			133.7			

	Series VIII.		Series IX.	Series X.
At. wt. of group.....	(150)	(147)	(149.5)	(153)
At. wt. of fractions.....	149.1	149.8	151.8	153.3
	151.3	142.8	153.2	153.0
			153.0	
			149.8	

The fractions had now become so small that it was considered advizable to combine them with fractions of the same atomic weight and absorption spectra, which had been obtained from the soluble double sulfate portion from monazite.

Series X showed a constant atomic weight of 153. The oxide had a light chamois color. The spectrum lines of a ten per cent. solution of the nitrate were:

Europium.		Samarium.		Erbium.	
464	strong	471, 478	faint	484.3, 486.8	fairly strong
534.5	strong	496.5, 500	haze	543.6, 545	fairly strong
592	faint	559	very faint	666	very faint

The earth was europium with only the faintest traces of samarium and a small amount of erbium.

Fractions from Series VIII and IX having the atomic weight of 149.8 were found to be constant. The absorption spectrum of a 20 per cent. nitrate solution was composed of strong lines of samarium, a few lines of erbium of medium strength, and one stronger one of praseodymium.

Samarium.		Erbium.		Praseodymium.	
463	faint	483–485	medium	595–604.5	strong
470–475	medium	542–544.8	medium		
497–501.5	strong	666.6	very faint		
531–535	medium				

The earth was therefore fairly pure samarium, being especially free from other members of the gadolinium group.

Soluble Double Sulfate Portion.—The earths remaining in solution after the removal of the insoluble double potassium sulfates, as described on page 1085, were precipitated as oxalates, converted into oxides and fractionated as chromates.[1] The earths of the first insoluble chromate fraction thus obtained (at. wt. 134) were separated as chromates into four

[1] Muthmann and Boehm, *Ber.*, 33, 42.

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fractions having the atomic weights 141, 145, 131, 122 in order of precipitation. Cerium was present in the first fraction and was separated as ceric hydroxide.

The first three fractions were fractionated as stearates, the atomic weights of the successive groups and fractions being:

SERIES A.

At. wt. of group.....	141	145	131
At. wt. of fractions.....	142.7	150.1	134.1
	143.5	150.0	133.1
	145.7	150.2	130.9
	139.4	146.3	...
	...	136.6	...

SERIES B.

At. wt. of group.....	143	146	150
At. wt. of fractions.....	149.6	150.8	153.2
	144.4	150.2	156.0
	...	147.9	147.8

SERIES C.

At. wt. of group...	...	...	150.5	147.8	144.4
At. wt. of fractions	154.0	152.2	154.0	154.7	151.0
	152.8	151.9	150.4	149.9	146.1
	151.5	148.9	151.8	146.0	134.6
	142.5	...	147.7	134.5	...

SERIES D.

At. wt. of group...	154	152.8	152.2	151.8	151.0	144.4
At. wt. of fractions	156.0	152.6	154.0	153.0	155.5	145.2
	153.3	152.5	151.4	151.0	151.8	143.0

Series D contained some of the most pure fractions from the insoluble double sulfate portion (page 1087) as well as those from Series C.

The second group of the series had an atomic weight of 152.8 and yielded two fractions of atomic weight 152.6 and 152.5. The limit of the efficiency of the stearate separation had therefore been reached for this particular earth in the quantity at hand—about three grams. Spectroscopic examination revealed the presence of a very slight trace of erbium, with a larger amount of samarium, although the atomic weight was near that of pure europium—152—, and the spectrum lines of this element are strong. The lines of the absorption spectrum of a 10 per cent. nitrate solution were:

Europium.		Samarium.		Erbium.	
465	faint	471	strong	484.3	faint
529	faint	478		486.8	
574.5	medium	498	medium		
592.6	strong			543	faint
597				546.5	
				666	

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Fractions having the atomic weight of 156 and 155.5 gave an absorption spectrum of erbium and samarium (extremely faint) with practically the same lines as above with varying intensity. The gadolinium was not so nearly pure as the europium.

Europium had therefore been obtained, which contained only the slightest traces of erbium, with a very small quantity of samarium, while by the same method (page 1087) another sample had been obtained which contained some erbium with only the slightest traces of samarium. There can be no doubt as to the efficiency of the stearate separation, although it did not appear advizable to effect the complete removal of erbium and samarium from the two samples of europium until larger portions of the earth could be obtained.

The samples of europium were obtained from the original monazite material after 59 series of fractionations yielding 204 fractions as shown below:

Double magnesium nitrates—1 series of 3 fractions.
Double potassium sulfates—1 series of 3 fractions.

Insoluble double sulfate portion.			Soluble double sulfate portion.		
Separated as	Series.	Fractions.	Separated as	Series.	Fractions.
Formates.....	7	21	Chromates.....	1	4
Stearates.....	32	120	Stearates.....	17	53
	39	141		18	57

Separation of Rare Earths from Gadolinite.—Rare earths were obtained from twenty-five pounds of gadolinite from Norway by treatment of the mineral with hydrochloric acid, and precipitation of the earths as oxalates from acid solution. The earths were fractionated into 18 portions as double potassium sulfates. The didymiums were practically all removed in fraction 12. The last three fractions yielded white oxides. The double sulfate fractions were converted into hydroxides which were then dissolved in formic acid. The 18 sulfate fractions were then divided by careful evaporation of the formate solution into 59 fractions. These were grouped according to the color of the oxide and absorption spectra into 8 groups, the atomic weights of which were afterwards found to be 138.6, 121.1, 108, 105, 102, 100, 98.6, 99.9.

The four fractions of higher atomic weights were fractionated as double potassium sulfate, the atomic weights being:

At. wt. of group.....	138.6	121	108	105
At. wt. of fractions.....	135	136	120.2	118.3
	...	...	107.8	107.4
	133	...	105.0	101.0

These fractions were combined according to their atomic weights and the three heavier groups, after removal of the cerium, were fractionated as stearates. The atomic weights were:

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At. wt. of group	136	135	133
At. wt. of fractions	138.2	136.1	140.9
	135	135.6	134.5
	127.2	124.8	...

The heavier fractions contained so small an amount of the earths desired in our work, erbium and samarium showing very faintly in the spectra, that the separation was not carried further.

Note.

The Stearate Separation of the Cerium Earths.—The effectiveness of the stearate separation when applied to the earths of the cerium group is shown by Series V (page 1086) where groups of the atomic weights of 140, 144, and 146 were fractionated. It is also indicated by certain groups in Series VII and IX in the insoluble sulfate portion, and by Series A, B, C, and D (page 1088) in the soluble sulfate portion.

Spectroscopic examination of the groups and fractions indicated a partial separation of the didymiums, while cerium was concentrated in the first fractions as shown by the hydrogen peroxide and ammonia test.

While none of the members of this group was isolated, the separations effected in this group, while seeking members of the intermediate group, leave little doubt as to the efficiency of the stearate separation in the cerium group.

Summary of Experimental Work.

After division as potassium double sulfate, the rare earths from monazite were fractionated as stearates, until the gadolinium earths were concentrated and separated. Eighteen series of 57 fractions from the soluble double sulfate portion yielded a fraction of constant atomic weight of 152.5 which was practically pure europium. A second sample of europium (atomic weight 153), containing a trace of erbium, was separated from the insoluble double sulfate portion by 39 series of 141 fractions. The separation at the same time yielded a sample of impure gadolinium of atomic weight 156, which contained some erbium, samarium, and europium, and also a sample of samarium of atomic weight 149.8.

The rare earths were extracted from twenty-five pounds of gadolinite and fractionated by 31 series of 129 fractions. The mineral contained quantities of the gadolinium earths too small to warrant their separation.

In the entire work 90 series of fractionations yielded 333 fractions, of which 159 were analyzed and the atomic weight of the earth determined.

Conclusions.

The experimental work described demonstrates that:

1. The gadolinium earths may be concentrated and separated by their fractional precipitation as stearates.

2. The stearate method is also applicable to the separation of the members of the cerium group.

MADISON, WIS.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 195.]

AQUA REGIA: PRELIMINARY PAPER.

BY WILLIAM C. MOORE.

Introduction.

There seems to be a wide-spread belief that the efficacy of the mixture known as aqua regia when used as an oxidizing agent is due to the free chlorine it may yield under certain conditions.[1]

Its action on a metallic sulfide, for instance, is generally expressed in accordance with this view, somewhat after the following manner:

$$3MS + 6HCl + 2HNO_3 \rightleftarrows 2NO + 4H_2O + 3MCl_2 + 3S \quad (1)$$

an equation obviously derived from the equation

$$3HCl + HNO_3 \rightleftarrows NOCl + 2H_2O + Cl_2, \quad (2)$$

first developed by Goldschmidt[2] to express the changes occurring when concentrated hydrochloric acid and nitric acid are mixed in the proper proportions and the mixture heated.

Lunge and Pelet,[3] however, in an investigation into the commercial methods for the preparation of chlorine, showed that when the chlorine from nitrosyl chloride formed by the above action from aqua regia at 100° was calculated to hydrogen chloride, and the nitrogen oxides were calculated as nitric acid there was too much of the former, and too little of the latter. These same investigators also showed that aqua regia becomes colored at 14°, begins to evolve gas at 35° and that between 95° and 100° a vigorous action occurs. When the temperature of the mixture was raised to 108.9° chlorine and other decomposition products were no longer evolved but a distillate containing an aqueous solution of hydrochloric and nitric acids was obtained. A study of the real nature of the course of oxidation reactions effected by aqua regia seems, however, to have been neglected. In seeking a full and consistent explanation of the action of aqua regia, the first question we have to answer is: "Is aqua regia always more effective than nitric acid as an oxidizer?" Böttger[4] mentions the general tendency of analysts to utilize aqua regia as an oxidizing agent, and without committing himself, hints that their faith in its efficacy may not always be well founded. It is obvious that in many cases it is a valuable reagent, and to explain why, in certain cases, it is so effective as an oxidizer and solvent Ostwald[5] has stated:

[1] Morgan, *Qual. Analysis*, p. 43, 1906 edition; Prescott and Johnson, *Qual. Analysis*, 5th edition, pp. 279, 333 (1904); Treadwell (Hall's translation), 1st edition, p. 247 (1905).

[2] Goldschmidt, *Ann.*, 205, 372 (1880).

[3] Lunge and Pelet, *Z. angew. Chem.*, 8, 3 (1905).

[4] Böttger, *Qual. Analysis*, trans. by Smeaton, p. 217 (1906 edition).

[5] Ostwald, *Principles of Inorg. Chem.* (Findlay's trans.), 3rd edition, p. 339 (1905).

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"The explanation is found in the consideration that the chlorine compounds which are formed of the above metals (gold and platinum) have a much more stable character than the nitrates which would be formed by the action of nitric acid. The fall from the initial substance to the end product is therefore greater in the case of aqua regia than in the case of nitric acid, not because aqua regia stands higher, but because the products of its action stand much lower." Thus, chloroplatinic acid possesses a smaller energy content than a possible platinic nitrate, so aqua regia dissolves platinum while nitric acid does not. But there are many cases where aqua regia is used to effect solution to which it is possible that such an explanation will not apply. It is obvious, for instance, that it holds perfectly good, with respect to the action of aqua regia upon mercuric sulfide; for mercuric chloride is much less highly ionized in aqueous solution than is mercuric nitrate;[1] but will it hold good for the action of aqua regia on lead sulfide, or upon such sulfides as arsenious, nickel and cobalt sulfides?

In the case of lead, lead chloride and lead nitrates are ionized at 25° to almost the same extent;[2] aqua regia and nitric acid each produce arsenic acid when arsenious sulfide is acted upon by either; cobalt and nickel chlorides are about as highly ionized as are their nitrates;[2] so if aqua regia in these special cases really is more effective as an oxidizer some other explanation than that free chlorine is the effective agent in aqua regia must be sought.

Again: a mixture of dilute nitric and hydrochloric acids, or of diluted "aqua regia" is sometimes used as an oxidizing agent; is chlorine set free from *these* mixtures?

If we write the reaction, (1) as separate equations in ionic form it becomes

$$2HNO_3 \rightleftarrows 2H^+ + 2NO_3^-$$
$$6HCl \rightleftarrows 6H^+ + 6Cl^-$$
$$8H^+ + 2NO_3^- \rightleftarrows 4H_2O + 2NO + 6(^+)$$
$$3MS\ (\text{solid}) \rightleftarrows 3MS\ (\text{dissolved}) \rightleftarrows 3M^{++} + 3S^{=}$$
$$6(^+) + 3S^{=} \rightleftarrows 3S\ (\text{solid}). \qquad (3)$$

It is also possible to include the following additional steps:

$$6(^+) + 6Cl^- \rightleftarrows 3Cl_2$$

and

$$3Cl_2 + 3S^{=} \rightleftarrows 6Cl^- + 3S\ (\text{solid}). \qquad (4)$$

Now, if the formulation of the action is correctly represented in the various steps of (3) it is at once apparent that the function of the hydrogen chloride is simply to furnish hydrogen ions. Simplified then, the essential features of (3) are depicted in the following scheme:[3]

[1] Ley, *Z. physik. Chem.*, 30, 247 (1899); Morse, *Z. physik. Chem.*, 41, 709 (1902).
[2] Kohlrausch and Holborn, *Leitvermögen*, p. 166 (1898 edition).
[3] This identical equation is given in Tower's *Qualitative Analysis* (1909 edition,

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$$4H^+ + NO_3^- \rightleftharpoons 2H_2O + NO + 3(^+) \qquad (5)$$

obviously the same scheme which expresses the action of nitric acid alone as an oxidizing agent when nitrogen dioxide is the only reduction product of the acid; in either case the three positive charges would be available to oxidize any substance, the oxidation product of which has a lower oxidation potential than nitric acid itself. In the case cited in (3), the sulfide ion is oxidized to elemental sulfur.

If, however, we include in the process the steps formulated in (4), the chloride ion actually does play a part in the oxidation, since according to this scheme the intermediate formation of chlorine and its subsequent reduction to chloride ion constitutes one of the essential steps. If this is true then the *chloride ion possibly acts as a catalytic agent.*[1] It has long been known[2] that a nitrate with hydrochloric acid, or a chloride with nitric acid, when heated behaves as does aqua regia; in fact, patents[3] have been obtained for the manufacture of chlorine by these processes.

In order to ascertain whether the ionic explanation outlined above is a legitimate one, the author has been conducting, for some time, a series of experiments upon the oxidation of various sulfides and other oxidizable substances. It must be stated at the outset that these experiments have in the main been conducted as preliminary experiments for the purposes of orientation. It is not possible, so far as the author is aware, to control the action either of nitric acid, or of any of the oxidation mixtures studied so that only one oxidation product of the sulfide ion is obtained, and so actual quantitative measurements of the rate of oxidation of sulfide ion, seem, for the present at least, out of the question. It is hoped, however, that a quantitative comparison of the effectiveness of nitric acid alone, and mixtures of nitric acid and hydrochloric acid as oxidizing agents can be made in some other way, such as by using some other substance than the sulfides so far studied.

Experimental Part.

Experiments on Mercuric Sulfide.—In order to study the comparative oxidizing effect of nitric acid alone, and that of mixtures in which the concentrations of the hydrogen and nitrate ion differed, a series of mixtures of nitric acid and sulfuric acid was prepared, and the action of mercuric sulfide of these mixtures and of nitric acid alone was studied. If possible, it would have been better to have used some stronger acid than

p. 14) to express the oxidation of ferrous to ferric ions, but apparently the author offers no explanation as to any difference that may exist between nitric acid and aqua regia as oxidizing agents.

[1] See, in this connection, Alex. Smith's "General Inorganic Chemistry," p. 448 (1096).

[2] See Gmelin-Kraut, Vol. 1, 3, p. 53 (1909).

[3] See Lunge and Pelet, *loc. cit.*

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sulfuric, but hydrogen iodide, which was thought of, itself acts on mercuric sulfide, while trichloroacetic, another possibility, could not be used on account of the low temperature at which it decomposes. In addition, the action on mercuric sulfide of mixtures, containing hydrogen, nitrate, and chloride ions in varying concentration, was superficially investigated.

These experiments with mercuric sulfide may be divided into three series: In Series A mercuric sulfide was treated with mixtures of nitric and sulfuric acids, in the cold (first, at 25.75° and then at room temperature). Where mixtures of 4 *N* nitric acid and 4 *N* sulfuric acid or 4 *N* nitric acid alone was used there was no apparent oxidation, even after many days. For instance, 4 *N* nitric acid had no effect after standing in contact with mercuric sulfide at ordinary temperature for 100 days. When a mixture of equal volumes of 4 *N* nitric acid and *concentrated* sulfuric acid was allowed to act on precipitated mercuric sulfide at 25.75° for 14 days some oxidation had occurred, as evidenced by the gray color of the solid and the brown gas in the upper part of the vessel. On standing at room temperature for 48 days longer this change in color of the solid was much more pronounced.

In Series B, mixtures of mercuric sulfide, 4 *N* nitric, and 4 *N* sulphuric acid were boiled, using a reflux condenser. Four-normal nitric acid effected the most rapid oxidation, then came in order: 66.7 per cent. 4 *N* sulfuric acid with 33.3 per cent. 4 *N* nitric acid mixture, then 33.3 per cent. 4 *N* sulfuric with 66.7 per cent. nitric acid, and lastly 4 *N* sulfuric acid alone.

In Series C, mercuric sulfide was boiled with mixtures containing hydrogen, nitrate, and chloride ions in varying proportions, a reflux condenser being used in each case, and the apparatus so arranged that any chlorine evolved would pass into 0.1 *N* silver nitrate acidified with nitric acid. A few details will probably be interesting:

Experiment 33.—0.5 g. HgS, 50 cc. 4 *N* HNO_3, 0.6 cc. 3 *N* KCl were boiled. Action began before the boiling point (105.1°) was reached; 5 min. after the heating began the action was vigorous and in 7 min. all the mercurous sulfide was oxidized to a light colored product. No indications of the evolution of chlorine were noted till after 44 min. of vigorous boiling when a slight cloud was produced in the silver nitrate. The yellow oxidation product weighed 0.42 g.

Experiment 34.—0.48 g. HgS, 40 cc. 4 *N* HNO_3, 0.5 cc. 3 *N* KCl were boiled under same conditions as in Exp. 33. Action began at 50°, with vigorous action at 95° ($1^1/_2$ min. after heating began), when the solid became yellow-gray in color. There were no indications of the evolution of chlorine. The residue weighed 0.54 g.

Experiment 38.—50 cc. of 4 *N* HNO_3 and 0.5 cc. 3 *N* KCl were boiled 30 minutes. There was almost no evolution of chlorine. The mixture was cooled, 1 g. of HgS added, and the heating resumed. A little action took place on adding the mercuric sulfide; there was brisk action 1 minute later, at 75°; 2 minutes after heating began, at 95°, brisk evolution of oxides of nitrogen, with no chlorine, and at 103.8° the solution boiled, 3 minutes after the heating began. The solid was partially oxidized.

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After 1 hour and 56 minutes' boiling the oxidation was not complete as there were still black particles left.

Experiment 41.—Practically a duplicate of No. 38; considerable chlorine evolved. In this experiment the preliminary boiling was omitted. In No. 42, 0.25 cc. 3 *N* HCl, 0.65 g. HgS and 50 cc. 4 *N* HNO_3 were boiled. In 41 minutes' boiling a large part of the sulphide was oxidized, and the oxidation was practically complete after 8 hours, and 47 minutes' boiling.

In all these experiments the mercuric sulfide employed was precipitated from a mercuric chloride solution, thoroughly washed and then dried before use.

Experiments with Lead Sulfide.—In the first set of experiments with lead sulfide, 0.5 g. precipitated lead sulfide was treated with 15 cc. *N* nitric acid; 0.5 g. was likewise treated with 15.0 cc. *N* nitric acid mixed with 0.25 cc. 3 *N* potassium chloride; and another 0.5 g. treated with 15.0 cc. *N* nitric acid and 0.25 cc. 3 *N* hydrochloric acid. Each of these mixtures was heated about 1 min. and allowed to stand one week. At the end of this time, the tubes in which chloride ion was present contained a mass of sulfur, permeated by crystals of lead chloride. The other tube still contained solid lead sulfide. In another set of experiments 0.25 g. lead sulfide was boiled (*a*) with 10 cc. 2 *N* nitric acid and 1 cc. 3 *N* hydrochloric acid; (*b*) with 10 cc. of 2 *N* nitric acid; and (*c*) 0.1 g. lead sulfide was boiled with 10 cc. 2 *N* nitric acid and 0.25 cc. 3 *N* potassium chloride. Again, the action was most rapid and complete in the cases where chloride ion was present. In each case a reflux condenser was used, and in all the experiments sulfur was deposited in the condenser tube. On repeating the experiments varying the concentration of the chloride ion, it was seen that the most sulfur was deposited in condenser tube of the flask containing the greatest concentration of chloride ion. Sulfate ions were produced in every case (precipitated as barium sulfate), and hydrogen sulfide was likewise evolved, as was shown by the precipitation of black silver sulfide when the evolved gases were passed through decinormal silver nitrate.

Experiments with Arsenious Sulfide.—When 0.185 g. of arsenious sulfide was heated, (*a*) with 50 cc. of 4 *N* nitric acid and (*b*) with 2.20 cc. 3 *N* hydrochloric acid, and 47.80 cc. of 4 *N* nitric acid, action began immediately in both instances. After heating 20 minutes only a little residue was left in either case. These mixtures were allowed to stand for two weeks, but no indications of further action were noted. In (*a*) the residue left weighed 0.04 g.; in (*b*) it weighed 0.06 g. 10 cc. of each mixture were taken and the arsenate ion determined by precipitation as magnesium ammonium arsenate, ignition and weighing as magnesium pyro-arsenate. In (*a*) the weight was 0.0415 g.; in (*b*) it was 0.0528 g.

When 0.1 g. of arsenious sulfide was treated with 20 cc. of 4 *N* nitric

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acid and 0.5 cc. 3 *N* potassium chloride, action began immediately, and on standing over night a sulfur-yellow residue, weighing 0.005 g. and consisting largely of sulfur, was left. A second experiment was performed at the same time, substituting 0.5 cc. water for the chloride solution; the yellow residue left had the color of arsenious sulfide and weighed 0 .045 g. Ten cc. of the solution from these experiments gave about the same volume of magnesium ammonium arsenate when precipitated under exactly the same conditions. These precipitates were not weighed.

Experiments on the Oxidation of the Ferrous Ion in Ferrous Ammonium Sulfate Solutions.—A series of experiments was carried out, in which tenth-normal ferrous ammonium sulfate was oxidized, (*a*) by means of nitric acid alone, (*b*) by means of solutions containing hydrogen, nitrate, and chloride ions in varying concentrations. The procedure was, in general, as follows: 25.06 cc. of 0.1 *N* ferrous ammonium sulfate were diluted to 45.06 cc. by means of the oxidizing solution; at definite intervals 10 cc. portions were removed and titrated with dilute potassium permanganate. When chloride ion was present, excess of manganous[1] ion ($MnSO_4$ solution generally) and excess of sulfuric acid was added, before titrating.

The temperature was ordinary room temperature (about 20°). In some of the series, one set of experiments was made (as will be seen) with nitric acid alone. The original titer for zero time was found by titrating 10 cc. of the ferrous solution before dilution, with the permanganate, and from the figure so obtained, the initial permanganate, value of 10 cc. of the 25.06 cc. of ferrous solution diluted to 45.06 cc., was calculated. All concentrations refer to total equivalent weights per liter.

SERIES A.

I. 25.06 cc. 0.1 *N* $FeSO_4(NH_4)_2SO_4$; 10 cc. *N* HNO_3; 10 cc. *N* HCl.
II. 25.06 cc. 0.1 *N* $FeSO_4(NH_4)O_2SO_4$; 20 cc. *N* HNO_3.

Time. Hrs.	I.	II.
0.0	5.89	5.89
5.5	6.00	5.80
23.0	5.87	0.85
29.25	5.92	0.45
47.00	5.71	0.18

Concentrations: Fe^{++} (*total*) 0.055; H^+ (total) 0.44 NO_3; I, 0.22; II, 0.44; Cl I, 0.22.

[1] See Zimmerman, *Ber.*, 15, 779 (1884); also Mixter and Dubois, THIS JOURNAL, 17, 405 (1895).

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SERIES B.

I. 25.06 cc. 0.1 N $FeSO_4(NH_4)_2SO_4$; 10 cc. N $FeCl_3$; 10 cc. N HNO_3.
II. 25.06 cc. 0.1 N $FeSO_4(NH_4)SO_4$; 10 cc. N HNO_3; 10 cc. N HCl.

Time. Hrs.	I.	II.
0	5.28	5.28
3.75	6.18	5.78
48	5.21	5.69
51.75	5.59	5.91
72	5.61	5.40

Concentrations: Total Fe^{++} I, II, 0.055. H^+, I, 0.22; II, 0.44; NO_3^-, I, II, 0.22; Cl^-, I, II, 0.22.

SERIES C.

25.06 cc. 0.1 N $FeSO_4(NH_4)_2SO_4$; 8.9 cc. N HNO_3; 11.1 cc. H_2O.

Time, hours.....	0.0	4.5	22.5	32.17
cc. $KMnO_4$.....	6.17	6.15	6.18	6.17

Concentrations: Fe^{++}, 0.055; H^+, 0.19; NO_3, 0.19.

SERIES D.

I. 25.06 cc. 0.1 N $FeSO_4(NH_4)_2SO_4$; 15 cc. N HNO_3; 5 cc. H_2O.
II. 25.06 cc. 0.1 N $FeSO_4(NH_4)_2SO_4$; 15 cc. N HNO_3; 5 cc. $N/1$HCl.
III. 25.06 cc. 0.1 N $FeSO_4(NH_4)_2SO_4$; 15 cc. N HNO_3; 5 cc. $N/$KCl.

Time. Hrs.	I.	II.	III.
0	5.83	5.83	5.83
4.57	0.50	5.96	5.95
65	0.10	5.96	5.99
109	0.00	..	6.00

Concentrations: Fe^{++} (total I, II, III), 0.055; H^+ I, III, 0.33; II, 0.44; NO_3^-, I, II, III, 0.033; Cl^-, II; 0.11 III, 0.33.

Experiments with Ferrous Chloride.—0.28 g. of pure iron wire was dissolved in 25 cc. of hot N hydrochloric acid. This solution was diluted to 100 cc. the next day. Three experiments were carried out. In I, 25.06 cc. of the ferrous chloride were mixed with 20 cc. of N nitric acid; in II, 25.06 cc. of the ferrous solution were mixed with 20 cc. 2 N nitric acid; in III, 25.06 cc. of the ferrous solution were mixed with 20 cc. 0.5 N nitric acid. 10 cc. of the original ferrous chloride were titrated with dilute permanganate, and from the number of cc. of this solution required for oxidation, the original or zero value for a 10 cc. portion of 25.06 cc. diluted to 45.06 cc. was calculated. At definite intervals 10 cc. portions of I, II, III were removed and titrated with permanganate, using excess of manganous sulfate and sulfuric acid as in the work with ferrous ammonium sulfate.

The temperature was that of the room—about 20°. The results for 10 cc. portions titrated as above, follow:

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Time (hrs.).	I. cc. $KMnO_4$.	II. cc. $KMnO_4$.	III cc. $KMnO_4$.
0	5.81	5.81	5.81
48	5.43	4.61	5.80
72	5.31	4.43	5.85
96	5.32	4.59	5.52

Discussion and Conclusions.

The results with mercuric sulfide show that mixtures containing hydrogen, nitrate and chloride ion more effectively and completely oxidize it than dilute nitric acid alone. This was to have been expected, from a knowledge of the great difference in the degree of ionization of mercuric nitrate and chloride. The formation of free chlorine, however, does not necessarily occur when such oxidizing mixtures as those just mentioned are heated, and if chlorine is set free it is largely, if not completely, reduced again to the ionic form. The results with hot mixtures of sulfuric and nitric acids show that if the total concentration of hydrogen ion is much greater than that of nitrate ion, such a mixture oxidizes mercuric sulfide more rapidly than a mixture where the opposite is true, which would be expected from a consideration of the active masses of the reacting substances. The difference noted, however, was slight.

Although lead sulfide is more rapidly oxidized by nitric acid when chloride ion is present than when it is absent, the difference in rate of oxidation might possibly be due to the difference in degree of dissociation of lead nitrate and lead chloride, the latter being less dissociated. For this reason, the experiments on arsenious sulfide have a greater value in the light they afford on the problem under consideration. The results with this substance show that in the cold a relatively greater amount of sulfur is formed by mixtures containing hydrogen, nitrate and chloride ion, from a given weight of arsenious sulfide, than is formed by the action of nitric acid alone; in hot solutions, while the weight of the *residue* is greater where chloride ion is present, likewise the amount of arsenate ion produced is greater than where nitric acid alone is used. The greater weight of the residue may be due to a relatively larger proportion of the sulfide ion being oxidized to sulfur by the diluted mixture containing chloride ion, while when nitric acid alone was used a greater amount of hydrogen sulfide could possibly have been formed. This point will bear further investigation.

The most important results are those obtained by oxidizing ferrous salts by means of mixtures containing hydrogen, nitrate and chloride ions, and by means of nitric acid alone. A glance at the tabulated results shows that oxidation is practically completely stopped in several of the experiments where chloride ion was present, and that nitric acid can oxidize ferrous sulfate more rapidly than ferrous chloride, because of this retarding action of the chloride ion. That the ferric ion retards

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the oxidation of ferrous in some cases is known[1] but this is hardly a case of that sort since nitric acid alone oxidizes ferrous solution in the cold easily, as is seen from the results above. This peculiar result will be thoroughly and carefully investigated.

Taking a survey of all of this preliminary work as a whole, it seems that there is some ground, then, for the following conclusions:

1. Dilute nitric acid and dilute mixtures containing hydrogen, nitrate and chloride ions may effect the oxidation of certain substances at different rates, even when the final products of the two oxidations do not differ in their energy content.

2. This difference may be due (*a*) to the influence of excess of hydrogen ions where chloride ion is absent, and (*b*) when chloride ion is present, to a possible catalytic action of this ion.

3. The most striking example of chloride ion acting as a catalytic agent is in the oxidation of ferrous salts, when it acts as a negative catalytic agent.[2] Finally it must again be emphasized that this work here reported is purely preliminary, and serves to outline a field of work in which it is hoped some important results may be achieved, in the future.

NEW YORK CITY.

A VOLUMETRIC ESTIMATION OF PHOSPHORIC ACID.

BY J. ROSIN.

Received April 26, 1911.

The reaction between silver nitrate and a soluble phosphate whereby silver phosphate is precipitated has served as the basis of several attempts at a volumetric estimation of phosphoric acid. Perrot,[3] who was the first to propose a method based on this reaction, precipitated the phosphoric acid with silver nitrate in the presence of acetic acid and determined the residual silver by sodium chloride. Holleman[4] converted the phosphoric acid or the mono-alkali salt into the dialkali salt by means of caustic soda and precipitated the phosphoric acid with silver nitrate in the presence of sodium acetate. The residual silver was then titrated in an aliquot portion by Volhard's method. Lieberman[5] adds a considerable amount of nitric acid to the solution of the phosphate, then adds an excess of silver nitrate and follows this with ammonia water until blue litmus paper is no longer affected. He then determines residual silver by Volhard's method.

Holleman's method recommends itself and it is in fact the best of the

[1] Benson, *J. Physic. Chem.*, 7, 1–14; 7, 356–77 (1903).

[2] See also in this connection, Benson (*loc. cit.*) with respect to the influence of iodide ion, and for other theories.

[3] *J. Soc. Chem. Ind.*, 1888, 311.

[4] *Z. anal. Chem.*, 1895, 85.

[5] *Analyst*, 1909, 361.

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methods above cited. However, results obtained by it are far from satisfactory. If a considerable excess of sodium acetate is used, silver acetate is co-precipitated and too high results are obtained. With a moderate excess only of sodium acetate, the acetic acid liberated, although very dilute, dissolves sufficient silver phosphate to yield results from 0.5–1 per cent. too low. It is evident that if phosphoric acid is to be completely precipitated, any free acid present must be neutralized.

The products resulting from the interaction of disodium hydrogen phosphate and silver nitrate are frequently represented in the text books by the equation:

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3. \quad (A)$$

Ostwald[1] and Treadwell[2] express the reaction by the equation

$$2Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3 + NaH_2PO_4. \quad (B)$$

Neither of these equations is correct. If a solution of sodium phosphate be precipitated with an excess of silver nitrate, the filtrate from the silver phosphate contains from 35–38 per cent. of the phosphoric acid originally used. According to equation (A) very little,[3] if any, phosphoric acid should be found in the filtrate, while according to equation (B) 50 per cent. of the original phosphoric acid should be found in the filtrate. If the filtrate from the silver phosphate is distilled after the excess of the silver nitrate has been removed by sodium chloride, very little nitric acid will be found in the distillate. In two experiments quantities of sodium phosphate which, according to equation (A) should yield nitric acid equivalent to 92.3 and 85.8 cc. 0.1 *N* caustic soda respectively, were precipitated with an excess of silver nitrate, the excess of the latter removed from the filtrate with a slight excess of sodium chloride, and the filtrate from the silver chloride repeatedly distilled with water into standard alkali, carrying the final distillation almost, but not quite, to dryness. Upon titrating the excess of alkali 3.40 and 2.95 cc. respectively of 0.1 *N* alkali were found to have been neutralized by the acid that had distilled over. This acid proved to be nitric acid. These facts show that the reaction will be represented more correctly if expressed by the equation

$$3Na_2HPO_4 + 6AgNO_3 = 2Ag_3PO_4 + 6NaNO_3 + H_3PO_4. \quad (C)$$

According to this equation no nitric acid is formed. The small quantities of it obtained in the experiments just described probably resulted from the action of the phosphoric acid formed, on the sodium nitrate, at the end of the distillation when the phosphoric acid became concentrated.

[1] "Principles of General Chemistry."
[2] "Qualitative Analysis."
[3] Enough silver phosphate will, of course, remain dissolved to maintain the equilibrium suggested by the equation.

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I have observed that when a solution of free phosphoric acid containing sodium nitrate is concentrated on the water bath, nitric acid is lost.

Equation (C) requires one-third of the original phosphoric acid to be found in the filtrate from the silver phosphate. The presence of more than one-third—35–38 per cent.—is probably due to the solvent action of the liberated phosphoric acid on the silver phosphate. The amount of silver phosphate dissolved is dependent upon the time of contact between it and the phosphoric acid.

That the reaction proceeds in the sense indicated by equation (C) was confirmed by the following experiment: 3.0164 grams of Na_2HPO_4 were precipitated with an excess of silver nitrate and made up to 202 cc.—allowing 2 cc. for the volume occupied by the silver phosphate (taking the specific gravity of silver phosphate to lie between 4 and 5) and filtered. From 100 cc. of the filtrate the excess of the silver nitrate was precipitated with a slight excess of sodium chloride, filtered, washed, and filtrate and washings, containing the free acid, divided into two equal parts. One part when titrated with 0.1 *N* alkali, using methyl orange as indicator, required 18.0 cc. The other part, with phenolphthalein as indicator, required 35.5 cc. With the latter indicator practically twice as much alkali was required. This is in accordance with the behavior of phosphoric acid towards these indicators.[1]

It is also seen that the quantity of alkali consumed corresponds almost theoretically to the amount required by equation (C)—17.7 cc. with methyl orange and 35.4 cc. with phenolphthalein. The fact that the filtrate from the silver phosphate is acid to methyl orange conclusively proves that equation (B) is incorrect, since according to this equation there is NaH_2PO_4 formed and this substance is not acid to methyl orange. The experiment just described was repeated several times and the same results obtained—with the phenolphthalein twice as much alkali was required as with methyl orange, and the amount of alkali corresponded very closely to that required by equation (C). The results of these experiments are presented here. The figures in the first line represent the amount of Na_2HPO_4 used for the quantity titrated.

	1.	2.	3.	4.
Na_2HPO_4 used, gram	0.7541	1.0322	0.8691	0.4346
Cc. 0.1 *N* KOH used, phenolph. ind.	35.5	48.5	41.5	20.6
Cc. 0.1 *N* KOH used, methyl orange ind.	18.0	24.5	20.1	10.2
Cc. 0.1 *N* KOH required by equation (C), phenolph. ind.	35.4	49.4	40.8	20.4
Cc. 0.1 *N* KOH required by equation (C), methyl orange ind.	17.7	24.7	20.4	10.2
Cc. 0.1 *N* KOH required by equation (A)	53.1	74.1	61.2	30.6

[1] See Ostwald "Scientific Foundations of Analytical Chemistry," Engl. edition, p. 128.

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While the method presented in this paper was being worked out, Wilkie[1] published a modification of Holleman's method. He neutralizes the phosphoric acid or its solution in nitric acid with caustic soda, using phenolphthalein indicator, adds an excess of 0.1 *N* silver nitrate and then runs in dilute caustic soda till just pink. He then adds 2 cc. 0.1 *N* H_2SO_4, makes up to volume and titrates an aliquot portion of the filtrate for residual silver by Volhard's method.

A procedure almost the same as Wilkie's was tried before Wilkie's method was published, but, on account of the precipitation of silver oxide when the alkali is added, the neutralization is difficult, as Wilkie himself admits, and failing to obtain a sharp end-point, I abandoned further attempts along this line. A method was sought where the use of sodium acetate could be avoided by neutralizing the free acid formed in the interaction of sodium phosphate and silver nitrate with a substance, a moderate excess of which would have no effect upon the excess of silver nitrate. Still under the impression that at least most of the acid is nitric acid, calcium carbonate at once suggested itself. It was, however, soon found that the precipitated carbonates of the alkaline earths, and even the naturally occurring carbonates of these earths, limestone, spar, strontianite and witherite, are transposed by silver nitrate solution into silver carbonate and the corresponding nitrate of the alkaline earth. Owing to their finer state of division, the precipitated carbonates are much more readily transposed than the natural. Precipitated basic zinc carbonate is also transposed, although slowly. Zinc oxide was tried and found to answer the purpose.

In a preliminary series of experiments with disodium hydrogen phosphate a rather large excess of zinc oxide was added, as it was thought that it would have no effect on the excess of silver nitrate. The results were too high and not in accordance with each other. The excess of the zinc oxide acts upon the silver nitrate, precipitating it as the oxide. Experiments have proven this. On allowing 0.2 gram of zinc oxide to stand in contact with 25 cc. 0.1 *N* silver nitrate for half an hour, 0.3 cc. of the silver nitrate was found to have been precipitated. Evidently a large excess of zinc oxide cannot be used.

The method as finally adopted, and which has given good results, is as follows: The solution of the phosphoric acid contained in a graduated (200 cc.) flask is neutralized, if necessary, to phenolphthalein, with caustic soda free from chloride,[2] an excess of 0.1 *N* silver nitrate added and the mixture well shaken. Zinc oxide, or a suspension of it in water, is then added little by little, shaking vigorously for two or three minutes after

[1] *J. Soc. Chem. Ind.*, 1910, 794.

[2] If chloride-free soda is not at hand, it can be neutralized with standard alkali of known chloride content.

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each addition and testing for free acid each time by dropping in a very small piece of blue litmus paper. When the color of the litmus paper is no longer affected, the solution is made up with water to the mark well mixed and allowed to subside for a few minutes. It is then filtered through a dry filter and the excess of the silver determined in an aliquot portion of the filtrate (100 cc.) by Volhard's method. Some of the results obtained by this method with sodium and ammonium phosphates and phosphoric acid are here given:

	P_2O_5 present. Gram.	P_2O_5 found. Gram.	Error. Gram.
1	0.0620	0.0618	—0.0002
2	0.0620	0.0622	+0.0002
3	0.0930	0.0928	—0.0002
4	0.0604	0.0604	0.0000
5	0.1208	0.1210	+0.0002
6	0.0613	0.0613	0.0000
7	0.0919	0.0916	—0.0003
8	0.0805	0.0807	+0.0002
9	0.1343	0.1342	—0.0001
10	0.2015	0.2018	+0.0003
11	0.0692	0.0692	0.0000
12	0.1037	0.1039	+0.0003

The points to be observed in this method are: (1) A minimum excess of 30 per cent. of the theoretical amount of silver nitrate required must be added, otherwise the results are apt to be too low. A large excess of silver nitrate, even as much as two and a half times the theoretical quantity required, does not interfere. (2) After the zinc oxide has been added, the mixture should not be allowed to stand long before filtering, as otherwise the excess of the zinc oxide—and an excess of the latter must necessarily be added in order to combine with all the acid—will precipitate some of the silver and thus vitiate the results. It is best to filter as soon as possible. The final volume to which the solution is made up has no effect. Using the same quantities of sodium phosphate and silver nitrate, but varying the final volume from 100–250 cc., no appreciable difference of results could be observed.

The method is available in the presence of sulfates, nitrates, chlorides and calcium, but cannot be used for the determination of the total phosphoric acid in the presence of more than traces of iron and aluminum. If a chloride is present, a correction must be applied.

Since, as has been shown, phosphoric acid is liberated in the interaction of sodium phosphate and silver nitrate, the action of the zinc oxide is probably this: it combines with the phosphoric acid, forming zinc phosphate which is then transposed by the silver nitrate into silver phosphate and zinc nitrate. This assumption has led to an investigation of the action of a solution of silver nitrate on the precipitated phosphates. The

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results may be summarized in the rough generalization that "precipitated phosphates soluble in acetic acid are transposed, more or less readily, by a solution of silver nitrate into silver phosphate and the corresponding nitrate, while those insoluble in acetic acid are not so transposed." Thus, the phosphates of the alkaline earths, magnesium, zinc, manganese, nickel, cobalt, copper and cadmium, are transposed, but those of iron, aluminum, lead and bismuth are not.

Quantitative examination of the action of silver nitrate on precipitated phosphates was limited to that of calcium, as this is the only phosphate that has any commercial value. It was found that precipitated calcium phosphate is quantitatively transposed into silver phosphate and calcium nitrate when it is shaken up for a few minutes with at least twice the theoretical amount of 0.1 *N* silver nitrate required. The procedure is the same as given under soluble phosphates. In case of the tri-basic phosphate, no zinc oxide is required, as there will be no acid formed. The commercial phosphate is usually a mixture of the di- and tribasic, and some acid will be formed when silver nitrate is added to it and consequently zinc oxide will have to be added. Below are given some results obtained by this method with two samples of calcium phosphate. Both contained chloride, which was determined and corrected for. The figures given in the first column were obtained gravimetrically.

	Per cent. P_2O_5 present.	Per cent. P_2O_5 found.	Error found.
1	47.20	47.12	—0.08
2	47.20	49.07	—0.11
3	48.52	48.36	—0.16
4	48.52	48.34	—0.18

The fact that the results obtained by this method are slightly lower than the gravimetric is probably due to the presence of a little iron in the phosphate.

The operation by the described method should not be performed in direct strong sunlight, as the yellow silver phosphate is liable to blacken somewhat and thus give rise to doubts as to the correctness of the procedure.

LABORATORY OF POWERS-WEIGHTMAN-ROSENGARTEN CO.,
ANALYTICAL DEPARTMENT, PHILADELPHIA.

THE OXIDATION OF FERROUS SALTS.

BY CHARLES BASKERVILLE AND RESTON STEVENSON.

Received April 26, 1911.

In the course of an examination of commercial oxygen, it was observed with surprise that a slightly acid solution of ferrous ammonium sulfate (Mohr's salt) was not appreciably oxidized by bubbling oxygen through it for three hours. Subsequent tests with variations were made and this communication records our findings.

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1. In the following instances, there was observed no oxidation of 5 g. Mohr's salt, as shown by titration with 0.5 N $KMnO_4$:

(*a*) The salt exposed to air for one week.

(*b*) Stream of oxygen for 3 hours through a solution acidified with sulfuric acid.

(*c*) Stream of filtered air for 3 hours through a solution acidified with sulfuric acid.[1] The same was observed with unfiltered air.[2]

(*d*) Stream of air for 3 hours through a neutral solution.

2. These four experiments were repeated, using $FeSO_4 \cdot 7H_2O$ instead of Mohr's salt, with the same results—no oxidation, thus showing that the presence of ammonium sulfate does not retard or accelerate the oxidation.

3. To determine the effect of the presence of substances which are ordinarily in iron ore, a hematite ore was dissolved in hydrochloric acid, precipitated by ammonium hydroxide redissolved in sulfuric acid, reduced by zinc and subjected to the following tests, no oxidation occurring in any instance:

(*a*) Without filtration, allowed to stand in an open casserole for 3 hours,[3] all of the zinc having dissolved.

(*b*) Filtered and allowed to stand in an open casserole for 3 hours.[1]

(*c*) Without filtration, a stream of air passed through for 3 hours.

(*d*) Filtered and a stream of air passed through for 3 hours.

4. The presence of other substances which are sometimes in iron ore has no effect upon the oxidation as was observed by passing air for 3 hours through solutions of Mohr's salt acidified with sulfuric acid to which had been added, in amounts corresponding to 0.1 g. of the metal, salts of these metals: Co, Cr, Cu, Mn, Mo, Ni, Ti, V, W.

5. The presence of undissolved substances was next tried. Dust in the air, glass wool, and pumice stone did not accelerate the oxidation, but when platinized asbestos was used, 5 g. of Mohr's salt in 200 cc. water, acidified with sulfuric acid, after a passage of air for 3 hours, showed about 50 per cent. oxidation, and in the absence of air no oxidation whatever.

6. Because the titration with 0.5 N $KMnO_4$ as in the experiments above does not detect small amounts of oxidation, standards of $Fe(CNS)_3$ were prepared and the solutions tested with potassium thiocyanate. In this way, it was shown that Mohr's salt (Kahlbaum), dissolved in water acidified with sulfuric acid and immediately tested, contains 0.0002 g. $\pm$ Fe^{+++} in the presence of 0.7100 g. $\pm$ Fe^{++}, and upon passing air through it for 3 hours there is a noticeable oxidation, and after 12 hours there has resulted a formation of 0.0001 g. $\pm$ Fe^{+++}. This

[1] No oxidation occurred after a passage of air for 12 hours and standing exposed to the air for 12 hours.

[2] The ventilation system of the building filters the air, but at times it is not entirely efficacious.

[3] After 30 hours, very little, if any, oxidation was observed.

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solution, after complete reduction by zinc, is oxidized in the presence of air, but at about the same rate as the original Mohr's salt in acid solution. The point of equilibrium is probably complete oxidation, but the reaction velocity in the absence of catalyzers is very small.

7. Oxidation of Fe^{++} readily occurs in alkaline solutions; 50 per cent. ± of the iron is oxidized upon passage of air for 3 hours.

8. All of these experiments were performed at room temperature. At a temperature slightly below the boiling point of the solution, upon passage of air for 3 hours, the Fe^{++} from the different sources was oxidized to an extent of about 2 per cent. in the acid solutions and about 5 per cent. in the neutral solutions.

Conclusion.—We conclude that Fe^{++} in acid and in neutral solutions, at room temperature, is so slowly oxidized, and this oxidation is so slightly affected by such substances as are apt to be present, that expulsion of air during reduction by zinc is unnecessary and the titration may be performed at leisure, in ordinary determinations of iron by titration with potassium permanganate.

COLLEGE OF THE CITY OF NEW YORK.

THE RAPID DETERMINATION OF SILVER AND CADMIUM BY MEANS OF THE GAUZE CATHODE AND STATIONARY ANODE.

BY RAYMOND C. BENNER AND WILLIAM H. ROSS.

Received April 17, 1911.

The use of the gauze cathode with stationary anode, which was found to be so efficient in the determination of nickel and cobalt,[1] has been extended to include the metals, silver and cadmium. The range of electrolytes from which these elements could be deposited on the gauze cathode in an adherent form, when strong currents were used, was found to be much less than in the case of the metals referred to.

Several of the electrolytes, which are applicable in case of the slow electrolytic methods, did not give good deposits on the gauze cathode with high currents, but the deposits obtained for each metal with potassium cyanide as an electrolyte were entirely satisfactory.

The electrodes used in these experiments were the same as those already described in the work on nickel and cobalt.[2]

Silver.—The first determinations of silver, using the gauze cathode, were made by Stoddard[3] with satisfactory results. The same experiments were repeated by Price and Humphreys.[4] They, however, reported rather unfavorably on the use of this method for the determination of silver,

[1] THIS JOURNAL, 33, 493.
[2] *Loc. cit.*
[3] THIS JOURNAL, 31, 385.
[4] *J. Soc. Chem. Ind.*, 29, 307.

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as the results which they obtained were always a little too low. In view of these conflicting results further work on the deposition of this metal was considered advizable.

The standard silver nitrate solution used in the following experiments was prepared by dissolving 1.5045 grams of C. P. silver foil in nitric acid. The excess of acid was then expelled on the water bath. The solution of the residue was made up to one liter and portions of 10 cc. containing 0.1504 gram of silver were taken for analysis. The purity of the foil had been previously established by careful analysis. Solutions of other concentrations were prepared by weighing out smaller portions of the silver foil, which were then converted into nitrate in the same way and electrolyzed directly.

A large number of experiments were made with a view of finding suitable electrolytes from which to deposit silver, but with the exception of potassium cyanide, none gave satisfactory results. Fairly good deposits were obtained from a warm solution of potassium persulfate, but the results were low, due to anodic deposition, on account of the strong oxidizing action of the solution. Electrolytes consisting of varying concentrations of nitric and other acids, as well as all of the electrolytes used

Amount taken.	Amount found.	Error, mg.	Amperes.	Volts.	Volume of solution, cc.	Time.	KCN. Grams.	KOH. Grams.
0.1504	0.1506	+0.2	2	5	50	25	8	2
0.1504	0.1508	+0.4	1	4.5	50	35	8	2
0.1504	0.1502	—0.2	4	5	50	15	8	2
0.1504	0.1505	+0.1	3	5	50	25	8	2
0.1504	0.1501	—0.3	3	5	50	25	8	2
0.1504	0.1508	+0.4	3	5	50	25	8	2
0.1052	0.1055	+0.3	3	5	50	30	8	2
0.1052	0.1056	+0.4	3	5	50	30	8	2
0.3156	0.3160	+0.4	3	5	50	25	8	2
0.1052	0.1052	±0.0	3	5	50	20	6	3
0.1052	0.1052	±0.0	3	5	50	25	6	2
0.2307	0.2305	—0.2	3	5	75	25	6	2
0.2360	0.2354	—0.6	3	5	50	25	6	2
0.2021	0.2014	—0.7	3	5	50	30	6	2
0.3563	0.3561	—0.2	3	5	75	30	6	2
0.3281	0.3284	+0.3	3	5	50	25	6	2
0.3048	0.3047	—0.1	3	5	50	25	8	2
			Rate of precipitation.					
0.1504	0.0508		3	5	50	2	8	2
0.1504	0.0877		3	5	50	4	8	2
0.1504	0.1154		3	5	50	6	8	2
0.1504	0.1312		3	5	50	8	8	2
0.1504	0.1462		3	5	50	12	8	2
0.1504	0.1474		3	5	50	15	8	2
0.1504	0.1506		3	5	50	20	8	2
0.1504	0.1504		3	5	50	25	8	2

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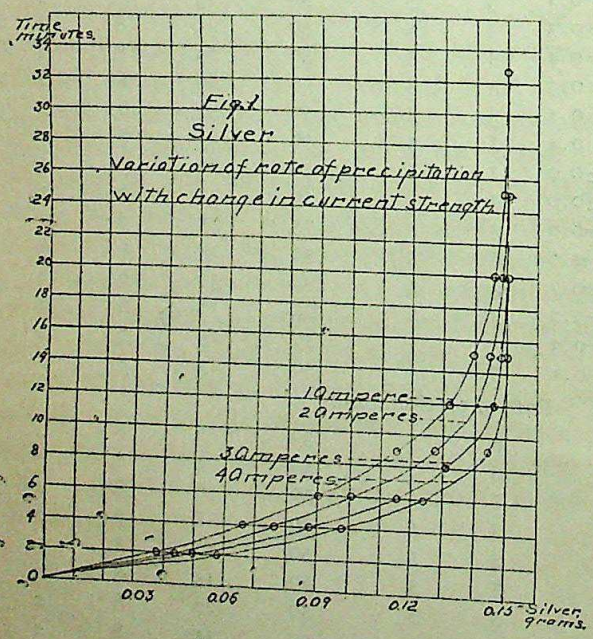
in connection with the deposition of nickel and cobalt, gave unsatisfactory results.

When carried out under the proper conditions, the deposits obtained from a solution of potassium cyanide were white in color and perfectly adherent. This electrolyte was very convenient to use, as the resistance of the solution was low and the conductivity did not change during the deposition of the metal. Consequently there was no tendency for the solution to boil over, even when currents as high as 5 amperes were used. When the cyanide only was used as an electrolyte, the solution became colored red as the electrolysis proceeded. This was prevented to a greater or less extent, when pure cyanide was used, by the addition of potassium hydroxide. The amount of hydroxide used (up to two grams in 50 cc. of solution) had but little effect on he rate of deposition. Larger amounts delayed the precipitation somewhat. The conditions under which the best deposits were obtained are given in the above table.

Careful qualitative tests were made at intervals, which showed that the precipitation of the silver was complete in the time given.

Before breaking the current at the end of the electrolysis the solutions were usually replaced with water, as otherwise the results obtained were usually a little low (about 0.4 mg. on an average).

When other conditions were the same the character of the deposit varied very decidedly with the amount of silver deposited. As the amount of silver increased, the deposit showed a greater tendency to sponginess. In order to get good results not more than 0.3 gram of silver should be deposited at one time on a cathode the size of the smaller ones used. When depositing amounts of silver weighing 0.15 gram, or less, from the concentrations of potassium cyanide given in the table, the strength of the current was found to have comparatively little effect on the character of the deposit and perfectly adherent deposits were obtained, even with currents of 5 amperes.



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Increasing the potassium cyanide decreases the rate of precipitation to a marked extent but the amount of silver which can be deposited in an adherent form may be correspondingly increased. For quantities of silver weighing less than 0.3 gram, 8 grams of potassium cyanide in 60 cc. of solution proved most satisfactory.

The effect of varying the strength of current on the rate of deposition may be seen from the curves in Fig. 1. For each ampere increase between 1 and 5 amperes, the time required to deposit 0.1504 gram of silver was decreased by about 5 minutes. This made the time for complete deposition of this amount of silver about twice as long with 1 as with 4 amperes.

The size of the cathode had a more important bearing on the character of the deposit than was noted for nickel and cobalt. The differences obtained by using cathodes of different sizes and by varying the amount of silver deposited may be seen in Figs. 2 to 4: Fig. 2, a microphotograph of a small section of the gauze cathode, weighing 6 grams, magnified 20 times, on which 0.1504 gram of silver was deposited, with a current of 3 amperes, from an electrolyte consisting of 8 grams of potassium cyanide in 60 cc. of water; Fig. 3, the same electrode upon which 0.4512 gram was deposited under the same conditions; and Fig. 4, the same amount of silver as shown in Fig. 3, deposited on the large cathode, weighing 16 grams, with the same electrolyte and current as were used to give the deposit shown in Fig. 1. The deposits shown in Figs. 2 to 4 were quantitative, and all appeared equally good to the naked eye.

Cadmium.—The rapid determination of cadmium by means of the gauze cathode and stationary anode has been made the subject of two previous studies.[1] Stoddard added just enough potassium cyanide to dissolve the precipitate formed, and deposited from 50 cc. of solution with a current of 5 amperes. Price and Humphreys used the same amount of potassium cyanide, depositing under the same conditions as used by Stoddard. In each case the results were satisfactory and obtained in a much shorter time than with other forms of stationary electrodes. As the same electrolyte was used in both cases it seemed advizable to repeat the work under varying conditions and try other electrolytes as well.

A standard solution was prepared by dissolving C. P. cadmium sulfate in water. The strength of this solution was determined by evaporating 10 cc. to dryness and weighing as the sulfate. This gave 0.1807 gram as a mean of 3 closely agreeing determinations. By the electrolytic method, using small currents and allowing the electrolysis to run over night, the mean of 5 determinations amounted to 0.1811 gram. The average of both methods of analysis gave 0.1809 gram as the cadmium content of 10 cc. of the solution.

[1] Stoddard, THIS JOURNAL, 31, 385; Price and Humphreys, *J. Soc. Chem. Ind.*, 29, 307.

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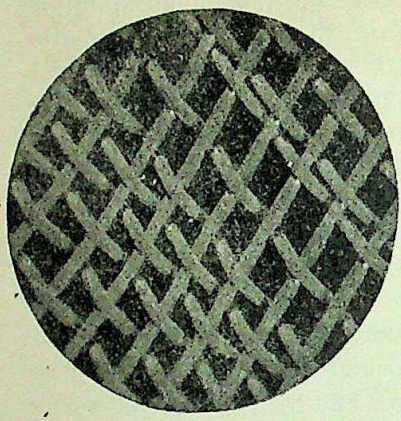

Fig. 2. × 20.

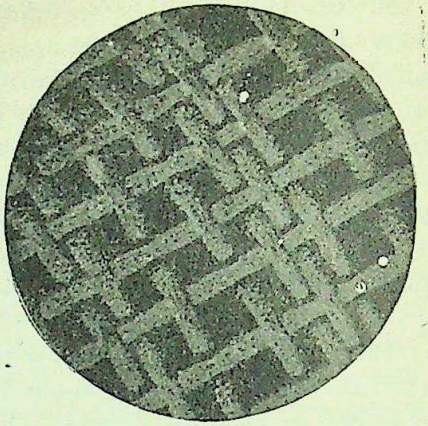

Fig. 3. × 20.

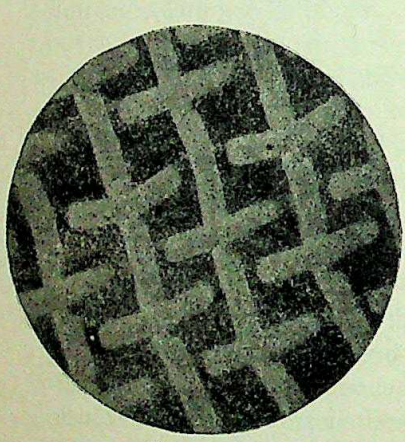

Fig. 4. × 20.

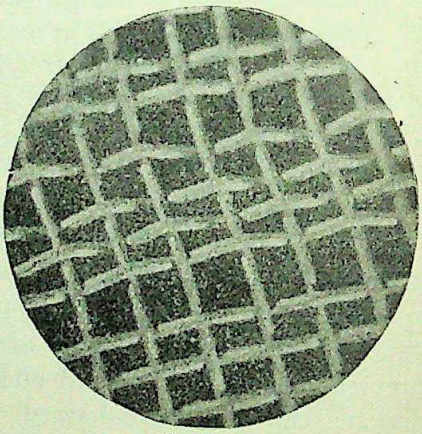

Fig. 5. × 20.

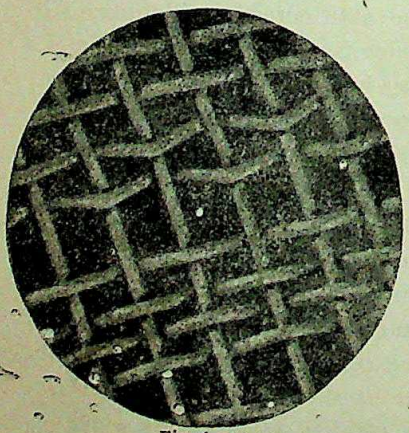

Fig. 6. × 20.

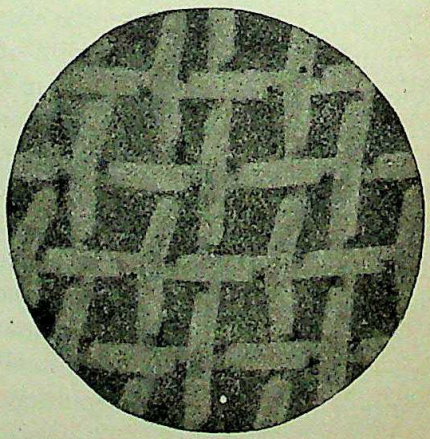

Fig. 7. × 20.

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The varying conditions under which it was possible to obtain good results with potassium cyanide electrolyte will be seen from the following table:

Amount taken.	Amount found.	Error, mg.	Amperes.	Volts.	Volume of solution, cc.	Time.	KCN. Grams.	KOH. Grams.
0.1809	0.1801	—0.8	4	5–6	60	30	5	1*
0.1809	0.1807	—0.2	4	5–6	60	30	5	1*
0.1809	0.1810	+0.1	4	5–6	60	30	5	1*
0.1809	0.1807	—0.2	3–4	5–7	60	30	5	1*
0.1809	0.1813	+0.4	3–4	5–7	60	30	2	1*
0.1809	0.1809	±0.0	4–5	6–7	60	30	5	2*
0.1809	0.1806	—0.3	4–5	8–11	60	30	KCN, enough	KOH, to
0.1809	0.1801	—0.8	4–5	8–11	60	30	to dissolve	alkalinity.
0.1809	0.1815	+0.6	4–5	8–11	60	30	ppt. formed.	"
0.1809	0.1807	—0.2	4–5	8–11	60	30	"	"
0.1809	0.1814	+0.5	4–5	8–11	60	30	"	"
0.3618	0.3623	+0.5	3–4	8–9	75	50	"	"
0.3618	0.3618	±0.0	3–4	8–9	75	50	"	"
0.3618	0.3616	—0.3	3–4	8–9	75	70	"	"
0.3618	0.3619	+0.1	3–4	8–9	75	70	"	"
				Rate of Precipitation.				
0.1809	0.0916		4	10–12	60	3	"	"
0.1809	0.1300		4	10–12	60	5	"	"
0.1809	0.1601		4	10–12	60	7	"	"
0.1809	0.1779		4	10–12	60	11	"	"
0.1809	0.1790		4	10–12	60	15	"	"
0.1809	0.1815		4	10–12	60	25	"	"

In cases where cadmium was precipitated from solutions containing no potassium hydroxide, the solution became colored by the decomposition of the cyanide. This was likely to make the results high but was prevented by the addition of a little potassium hydroxide as in the case of silver. As cadmium is somewhat soluble in potassium cyanide solutions, it was found necessary to wash before the current was broken in cases where strong solutions were used. The deposits were at all times uniformly bright and adherent. When examined under the microscope it was seen that an occasional deposit showed a tendency to sponginess but, notwithstanding this, good quantitative results could always be obtained.

Varying the concentrations of the cyanide had much less effect on the character of the deposit obtained than was noted for silver, as may be seen in the microphotographs: Fig. 5, a section of the smaller cathode upon which 0.1815 gram of cadmium had been deposited with a current of 5 amperes from 75 cc. of an electrolyte made by adding just enough potassium hydroxide to the cadmium sulfate solution to make it alkaline and then enough potassium cyanide to dissolve the precipi-

* Washed before breaking the current.

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tate formed; Fig. 6, the same electrode on which 0.1508 gram of cadmium was deposited from an electrolyte containing 2 grams of potassium hydroxide and 6 grams of potassium cyanide in 75 cc. of solution with a current of 5 amperes; and Fig. 7, a section of the larger electrode upon which 0.1812 gram of cadmium had been deposited under the same conditions as the deposit shown in Fig. 5.

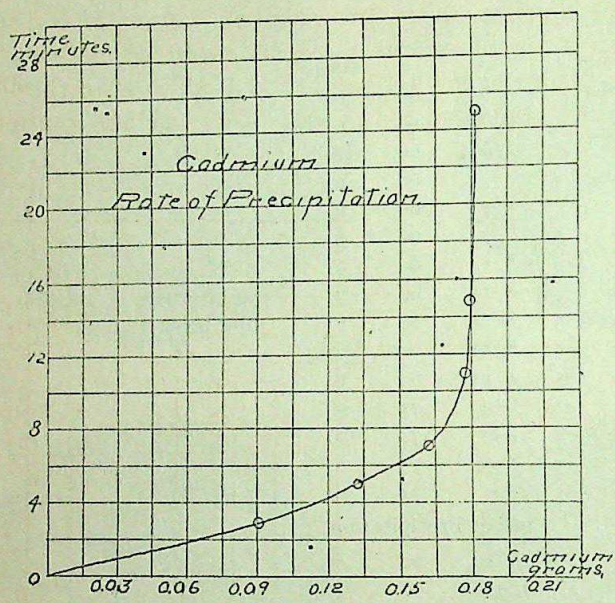

Fig. 8.

In addition to the experiments with potassium cyanide many others were made with other electrolytes, with the same negative results, as mentioned in the case of silver.

The anodes were weighed at the end of a number of consecutive electrolyses of both silver and cadmium in which the cyanide electrolyte was used to determin to what extent they decreased in weight. This appeared to be very slight, amounting to 0.1–0.2 mg. on an average for an electrolysis running from 20 to 30 minutes. The cathodes decreased in weight at about the same rate.

UNIVERSITY OF ARIZONA, TUCSON.

A MODIFIED COLORIMETER AND SOME TESTS OF ITS ACCURACY.

BY EDWARD DEMILLE CAMPBELL AND WILLIAM B. HURLEY.

Received May 18, 1911.

In a colorimeter for general use, simplicity in construction and operation, and accuracy in reading are the principal features to be sought.

In the colorimeter described below the means of observing the colors is in principle the same as that employed in the colorimeter described by W. G. Smeaton in THIS JOURNAL, 28, 1433, although the construction has been simplified by using two half-mirrors permanently fixed at an angle of 45° instead of mirrors adjusted by springs.

The tubes for holding the solutions to be compared are those of one of the well-known colorimeters in which the unknown solution is placed

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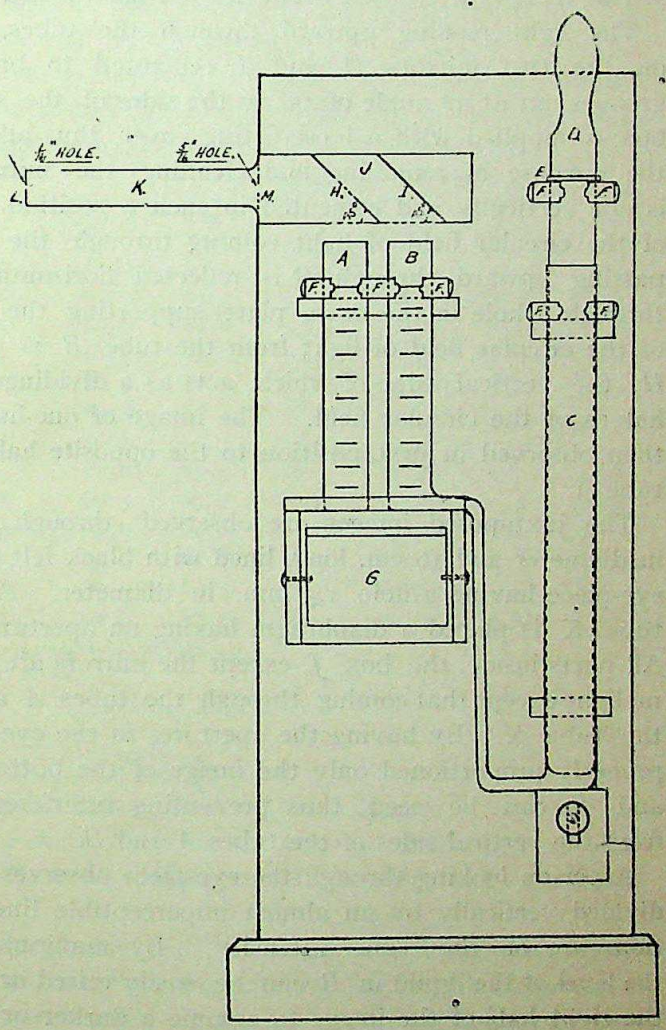
in the left-hand tube while the color is matched by raising or lowering the level of a standard solution in the right-hand tube by means of a glass plunger working in an attached reservoir.

The accompanying diagram shows the essential features of construction of the colorimeter employed in the tests described below. The unknown solution is placed in the left-hand tube *A* which is 19 cm. long, 3 cm. in diameter, and graduated for 15 cm. The standard solution is placed in the right-hand tube *B* which is the same size as *A*, the graduated portion being divided into 100 divisions of 1.5 mm. each. The tube *B* is permanently connected by a glass tube with the reservoir *C* in which the glass plunger *D* works, so that the level of the liquid in *B* can be readily controlled by raising or lowering the plunger. As the tube *B* and reservoir *C* are made in one piece, the liquid used for the standard solution comes in contact with glass only, thus preventing any possibility of chemical change due to contact with the container. The plunger is provided with a rubber collar, *E*, so placed as to prevent the plunger from accidentally striking and breaking the bottom of the reservoir. The tubes *A* and *B*, with the connecting reservoir, rest on wooden supports, the one under *A* and *B* being provided with holes for the passage of the light, and are held in position by spring clips, *F F*. This arrangement allows the glass parts to be



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readily removed for cleaning and filling. The light for illuminating the solution is reflected upward through the tubes *A* and *B* by means of the adjustable mirror *G*. The best results are obtained by facing the colorimeter toward a north window in order to get reflected sky-light through the tubes, care being taken to avoid light reflected from adjacent objects. The black wooden back of the colorimeter serves the double purpose of a support for the parts of the instrument and of a screen, as it is interposed between the color tubes and the source of light.

The light passing upward through the tubes, *A* and *B* impinges on the two mirrors *H* and *I* cemented to brass plates sliding in grooves cut at an angle of 45° in the sides of the wooden box *J*. This box is supplied with a loose-fitting cover, thus allowing easy access for the purpose of removing and cleaning the mirrors. The mirror *H* is cut vertically and cemented in such a position as to reflect one-half of the circular field of light coming through the tube *A*. The light passing upward through *B* is reflected horizontally by the mirror *I*, through a hole in the brass plate supporting the mirror *H*. One-half of the circular field of light from the tube *B* is cut off by the mirror *H*, the vertical edge of which acts as a dividing line between the two halves of the circular field. The image of one-half of the tube *B* is then observed in juxtaposition to the opposite half of the image of the tube *A*.

The juxtaposed images are observed through a tube, *K*, 2.5 cm. in diameter and 16 cm. long, lined with black felt and provided with an eye-piece having a hole 1.5 mm. in diameter. At the point *M* in the tube *K* is placed a diaphragm having an aperture 8 mm. in diameter. All parts inside the box *J* except the mirrors are painted black so that no light except that coming through the tubes *A* and *B* passes through the tube *K*. By having the apertures in the eye-piece and diaphragm properly proportioned only the image of the bottoms of the tubes *A* and *B* can be seen, thus preventing interference of light reflected from the vertical sides of the tubes *A* and *B*.

A person looking through the eye-piece observes a single circular field divided vertically by an almost imperceptible line when the two solutions are of the same intensity. By manipulating the plunger *D*, the level of the liquid in *B* can be easily raised or lowered, thus causing the right half of the image to assume a darker or lighter shade at will. In matching colors with an ascending column in *B*, that is, gradually deepening the color of the right half of the field, the usual tendency is to stop a little below the true reading while in a comparison with a descending column the opposite is the case.

In an article entitled "Sensitiveness of the Colorimetric Estimation of Titanium" in THIS JOURNAL, 33, 504 (1911), Roger C. Wells describes

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a method for the determination of the sensitiveness of the colorimeter devised by George Steiger, of the U. S. Geological Survey, and described by him in THIS JOURNAL, 30, 215 (1908). In order to determine the sensitiveness of the colorimetric estimation of titanium by means of the colorimeter described above, solutions similar to those employed by Wells were prepared. After the color produced by the action of hydrogen peroxide on each titanium solution had been developed, the tube *A* was filled to a depth of about 9 cm. with a portion of this solution. The remainder of the solution was placed in the tube *B* and reservoir *C*. The exact level of solution in tube *A* was then noted and ten readings, five on an ascending column and five on a descending column, were made. The results of these comparisons are given in the subjoined table:

Exp No.	Conc. $MgTiO_2$ in 100 cc.	Color seen through column 9 cm. deep.	Setting of L. H. Col'n. A.	R. H. column B. Max. read.	Min. read.	Av. of 10 read.	Per cent. max. variation.	Per cent. error of avs.
1	0.30	Very slight	61.0	62.0	51.0	57.1	9.6	6.80
2	0.60	Light straw	60.0	64.0	57.0	60.05	5.8	0.08
3	1.00	Good straw	60.0	61.0	57.0	59.35	3.4	1.25
4	1.30	Pale lemon	60.3	61.0	59.0	59.90	1.7	0.66
5	1.6	Pale lemon	60.0	62.0	59.0	60.30	2.5	0.50
6	2.5	Lemon	60.5	62.0	58.0	60.30	3.3	0.33
7	4.0	Yellow	60.5	62.5	58.0	60.00	3.75	0.83
8	5.0	Yellow	61.0	63.0	58.5	60.90	3.7	0.16
9	8.4	Dark yellow	60.5	63.0	60.0	61.70	2.4	1.98
10	10.0	Dark yellow	60.0	61.0	58.0	60.00	2.5	0.00
11	11.2	Dark yellow	59.5	61.0	58.5	60.15	2.08	1.09
12	15.0	Good orange	60.0	62.5	59.0	60.30	2.9	0.50
13	20.0	Dark orange	60.0	62.0	58.0	60.15	3.3	0.25

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.

NOTES.

Analysis of Aboriginal Copper Objects from Mexico and Yucatan.—The following analyses were made at the request of Professor F. W. Putnam, of the Peabody Museum of American Archaeology and Ethnology of Harvard University.

The objects to be analyzed were four small copper bells, about 3.5 cm. long, and about 2 cm. in diameter, weighing in the neighborhood of 5 grams. Owing to their weathered condition and the thinness of the metal, it was impossible to obtain a fair sample of the metal without some oxide, but nevertheless the analyses show that the original metal must have been very pure. Any impurities in the original metal would have appeared in the analyses, because weathering would not have removed them to an appreciable extent. The bell designated as C was in the best condition, and it is probable that a clean sample of the metal

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was obtained for analysis. As a check on the procedure, an analysis was made of a piece of modern sheet copper.

The procedure in all cases was as follows: About 1 to 2 grams of metal were cut off, cleaned by scraping, weighed, and dissolved in strong nitric acid. The solution was then made up to 100 cc. and aliquot parts taken for the qualitative and quantitative analyses. The residue insoluble in nitric acid, which in every case but one weighed less than 0.001 gram and in that one case weighed a little less than 0.01 gram, was insoluble in yellow ammonic sulfide but was partially soluble in aqua regia, leaving a gritty residue. The residue weighing about 0.01 gram was from the metal of bell A, which was very friable and full of minute cracks impossible to clean out entirely. This residue left a much larger proportion insoluble in the acid, probably siliceous material. The aqua regia solution gave a test for gold with stannous and stannic chlorides, and also with ferrous sulfate.

In the course of the qualitative analysis, the sulfide precipitate, supposed to contain the arsenic and copper groups, was found to be insoluble in ammonic sulfide, showing absence of arsenic. Bismuth and cadmium were absent in every instance, and lead was found only in the bell from Mexico. After the precipitation of the sulfides of the copper group, the filtrate was evaporated to dryness, leaving a hardly appreciable residue which gave a test for iron.

In the quantitative work, the method described by Richards and Bisbee[1] was employed for depositing the copper electrolytically. The lead was determined as lead sulfate. The iron was not present in sufficient quantity to give a significant weight. There was no significant residue on evaporating the residual solution.

Bell.	Condition.	Cu. Per cent.	Fe.	Ag.	Au.	Pb. Per cent.	SiO_2.	O, CO_2, etc., by difference. Per cent.	Origin.
A	Deeply corroded.....	80.2	trace	trace	trace	....	trace	19.8	Yucatan
B	Fair.....	96.4	trace	....	trace	....	trace	3.6	Yucatan
C	Good.....	99.7	trace	trace	trace	....	trace	0.3	Yucatan
D	Fair.....	76.7	trace	trace	trace	19.3	trace	4.0	Mexico
	Modern sheet copper.	100.0	trace	....	....	....	....	...	

A. H. FISKE.

HARVARD UNIVERSITY,
CAMBRIDGE, MASS.

The Analysis of Nitrous Oxide.—On attempting to analyze nitrous oxide as supplied in cylinders in the liquid state, we found ourselves confronted with certain difficulties. Consecutive samples of the gas, as drawn off from the cylinders, will vary somewhat in composition, apparently for the reason that the impurities (oxygen and nitrogen) are in

[1] THIS JOURNAL, 24, 530 (1904).

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solution in the liquid nitrous oxide and the sample of gas as drawn or may not have reached a state of equilibrium with the liquid. This evidently will depend on the rate at which the sample is drawn, the length of time elapsing between drawing samples, and various other factors. Duplicate results can easily be obtained from a sample large enough for several analyses but there is no certainty as to what such a sample represents. Again there is a regular progressive change in the composition of the samples as drawn from the cylinder. The impurities escape at a more rapid rate proportionally than the nitrous oxide in which they are dissolved and the nitrogen escapes faster than the oxygen. Below are three sets of figures obtained from the same cylinder of material.

	True content of cylinder.	Nearly full.	Nearly empty.
Per cent. O_2	1.4	2.9	0.7
Per cent. N_2	5.2	11.2	1.6
Per cent. N_2O	93.4	85.9	97.7

We find that all these difficulties can be avoided by the simple expedient of inverting the cylinder and drawing a sample from the bottom of the liquid. That this method gives a fair sample we have proved by drawing a sample in this manner and comparing the result obtained from this sample with that obtained by taking samples at regular intervals during the escape of a whole cylinder of the gas, plotting the results obtained from these samples on rectangular diagram paper and calculating percentages from the areas so obtained.

	From inverted cylinder.	From diagram.
Per cent. O_2	1.1	1.0
Per cent. N_2	3.1	3.3
Per cent. N_2O	95.8	95.7

Oxygen was determined by absorption with pyrogallate, nitrous oxide by explosion with hydrogen, and nitrogen by difference. No impurity other than oxygen and nitrogen was detected in the four cylinders examined except in one specimen, which contained a small amount of carbon dioxide.

The variation in composition in the gas as drawn from the cylinder must be of significance in the administration of the gas, and the method of getting a fair sample should be applicable to other liquefied gases such as carbon dioxide and ammonia.

W. R. SMITH,
E. D. LEMAN.

LEWIS INSTITUTE, CHICAGO,
May 8, 1911.

On the Qualitative Detection of Mercury by the Method of Klein.—In the work in qualitative analysis at Columbia University, the student is required to report not only what cations and anions are present, but also the approximate concentrations of nearly all the ions tested for. The

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concentrations may have one of several definit values. Twenty-five cc. of the "unknown" are taken for analysis, and a comparison test on 25 cc. of a standard solution of the ion tested for is carried out as each confirmatory test is made. This method of procedure, introduced at Columbia by Assistant Professor H. T. Beans, has, in general, yielded excellent results even in the hands of inexperienced students.

In confirming mercury, in either state of oxidation, however, difficulty has been experienced in getting the concentrations with sufficient accuracy. This was because the group precipitates of both mercurous and mercuric ions were dissolved in *aqua regia*; then after evaporation, a confirmatory test was made by reducing to metallic mercury by means of stannous chloride. This method, as is well known, yields colloidal mercury, which is difficult to filter, and does not separate readily in a form suitable for making comparison tests.

It occurred to the author that this obstacle to the consistent application of the analytic procedure in use here might be overcome by a reversal of the process used in making the Nessler test for ammonia, *i. e.*, to test for mercury by means of a mixture containing potassium iodide, sodium hydroxide, and ammonium hydroxide.

After some experimental work on the method had been carried out, it was found that this method had already been proposed by Klein;[1] however, it does not seem to have been used at all in the qualitative detection of mercury, so it is here presented in order that attention may be called to the certain and positive results it yields in the hands of beginners in qualitative analysis.

Preliminary experiments showed that with a mixture containing 10 cc. tenth-normal potassium iodide, 10 cc. 2.5 normal sodium hydroxide and 10 cc. 3 normal ammonium hydroxide, a reagent was at hand, a few drops of which would yield a very decided reaction immediately with 5 cc. of a solution containing mercuric ion of ten-thousandth normal concentration, while 5 cc. of hundred-thousandth normal mercuric ion gave a slight turbidity on standing, when a few drops of this reagent were added.

As the unknowns assigned for analysis contain mercury in much greater concentration than these low concentrations, the amount and concentration of the potassium iodide was changed; a little experimentation showed that it was best to use 5 cc. of half-normal potassium iodide with 10 cc. of three-normal sodium hydroxide and 10 cc. of three-normal ammonium hydroxide; 25 cc. of this reagent give an immediate precipitate of red-brown "Nessler's precipitate," with 25 cc. of 0.001 *N*, 0.01 *N*, or 0.1 *N* mercuric chloride; and a mixture of the oxide and the above

[1] Klein, *Arch. Pharm.*, [3] 27, 73 (1889); see also Denigès, *Chem.-Ztg.*, 20, 70 1896).

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compound with 25.0 cc. of 0.5 *N* mercuric chloride. The precipitate settles rapidly, and there is no difficulty in making comparison tests.

To adapt the method for class use, the following directions were formulated:

"Dissolve the residue of mercury and amido mercuric chloride (Group I)[1] or the residue of mercuric sulfide, and double sulfide and nitrate ($Hg_3S_2(NO_3)_2$) (Group II)[1] in *aqua regia*, and evaporate nearly to dryness, *i. e.*, till only 0.5 to 1.0 cc. of liquid is left. Add 10 cc. water and filter. Wash the residue, if any, with two portions of water, each 2.5 cc. in volume, adding to the filtrate. Now add to this filtrate 10 cc. three-normal sodium hydroxide, and then 25 cc. of the following mixture: 10 cc. three-normal sodium hydroxide, 10 cc. three-normal ammonium hydroxide and 5 cc. half-normal potassium iodide. Red or brown-red precipitate indicates mercury. Make comparison tests by adding 25 cc. of the above test reagent to 25 cc. of a mercuric chloride solution of known concentration since a 25 cc. portion of the unknown was used for analysis."

In the hands of students having had absolutely no experience in the detection of mercury, this method has yielded excellent results where ordinary care and intelligence has been exercised. The main points to note are that the excess of *aqua regia* must be removed and that the mercuric chloride must not be volatilized by overheating the solid residue left on evaporation. In laboratories where concentrations are not reported by the students, the alkaline ammoniacal iodide solution should be added drop by drop, taking care, however, that the solution to be tested is neutral or alkaline before making the test.

WILLIAM C. MOORE.

QUALITATIVE LABORATORY,
COLUMBIA UNIVERSITY, NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONSTITUTION OF DEHYDROACETIC ACID.

BY WILLIAM J HALE.

Received April 22, 1911.

The construction of a satisfactory structural formula for dehydroacetic acid has occupied the attention of chemists ever since its discovery by Geuther[2] in 1866. He obtained this crystalline substance from the decomposition products of acetoacetic ester, but attempted nothing beyond its empirical formula, $C_8H_8O_4$. The determination of its correct structure has become highly important by reason of the great variety of well-known and important compounds that can readily be prepared from it, such, for

[1] See Böttger's "Qualitative Analysis," Smeaton's translation, 1906 ed., pp. 9 and 24 for analysis on this point.

[2] *Jena'sche Zeitschrift*, II, 387 (1866).

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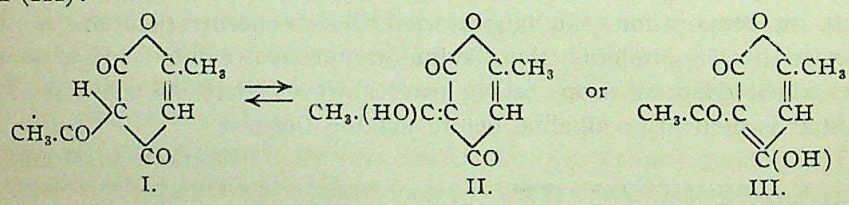
example, as diacetyl acetone, lutidone, dimethylpyrone, and others. No doubt much of the difficulty that confronted the correct interpretation of observations with this acid lay in the possible existence of two ionizable hydrogen atoms. Ordinarily there is but one acid hydrogen, a hydrogen linked to a carbon atom which is adjacent to three carbonyl groups, yet when this hydrogen is replaced by a methyl group a second acid hydrogen makes its appearance.

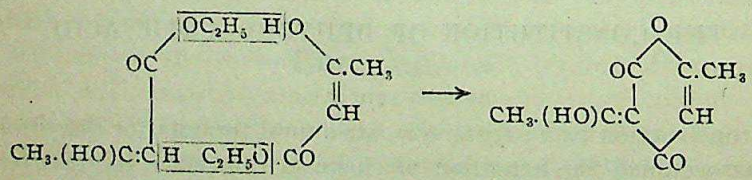
The formula proposed by Oppenheim and Precht,[1] as well as that by Haitinger[2] and also by W. H. Perkin, Jr.,[3] accounted for this acidity, through the presence of a carboxyl group. Ostwald[4] showed that this assumption was entirely unfounded by reason of the small dissociation constant (K = 0.00053) and proposed for the acid a formula according with monoacetyltriketohexamethylene, an hypothesis, however, which could not be substantiated by experimental evidence.

Schibbye[5] even supposed this acid to have a structure in the form of an eight-membered ring.

In 1890 Franz Feist[6] proposed his "wahre Constitutionsformel"[1] for dehydroacetic acid. In this we have a derivative of pyronone (a keto-dihydropyrone) of the constitution (I), or a 6-methyl-3-acetopyrononе; a compound which may also present two possible tautomeric forms (II) and (III):



The acid is, therefore, to be considered as a δ-lactone and produced (in tautomeric form) from two molecules of acetoacetic ester in the following manner:



In 1891 J. Norman Collie[7] proposed a formula (IV) for dehydroacetic

[1] *Ber.*, 9, 323 (1876).
[2] *Monatsh.*, 6, 103 (1885); *Ber.*, 18, 452 (1885).
[3] *J. Chem. Soc.*, 51, 484 (1887).
[4] "Ueber die Affinitätsgrössen organischer Säuren und ihre Beziehungen zur Zusammensetzung und Constitution derselben," W. Ostwald, Leipzig, 1889.
[5] Inaugural Dissertation, Würzburg, 1882.
[6] *Ann.*, 257, 253 (1890).
[7] *J. Chem. Soc.*, 59, 179, 617 (1891).

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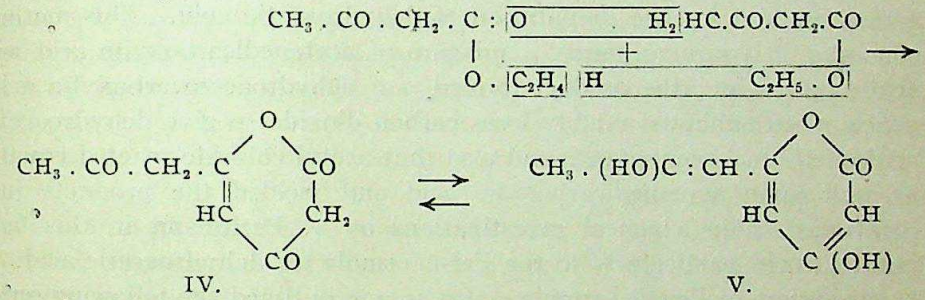
acid somewhat different from that of Feist's. An acetonyl group is here considered as a side-chain in the α-oxypyrone (or pyronone) ring. This constitutes a 6-acetonylpyronone and differs from Feist's formula only in respect to the acetyl group, which now is considered as replacing a hydrogen atom of the methyl group in the 6-position as shown by Feist. The basis for this formula rests upon well substantiated evidence for the possible condensation of the oxygen of an acetyl group with two hydrogen atoms of a methyl group adjacent to a carbonyl. The application to acetoacetic ester may be looked upon (according to Collie) as proceeding in the following manner:



The presence of ethylene is usually detected in the decomposition of acetoacetic ester, hence its occurrence was thought to be accounted for most simply by the reaction just given. Feist[1] later pointed out the important fact that when also a methylene group is present and adjacent to a carbonyl group there is not so marked a tendency for the methyl group to enter into condensation.

The Collie formula adequately explained all of the reactions in which dehydroacetic acid had so far been concerned. It satisfactorily accounts, in its tautomeric form (V), for the formation of a dichloride (by action of phosphorus pentachloride), where apparently two hydroxyl groups are replaced by chlorine. The slight acidity noted in the monomethyl ether of dehydroacetic acid may likewise be attributed to the possible existence of the second hydroxyl. The Feist formula can only account for one possible chloride by replacement of an hydroxyl group. This failure to explain the formation of a dichloride has indeed been one of the strongest arguments against the Feist formula. Feist,[2] however, has stated that the formation of the dichloride is by no means a simple process, but presumably one in which the ring itself is opened, as is the case when ammonia and amino-derivatives react upon this acid.

The production of dehydrobenzoylacetic acid,[3] by prolonged heating of benzoyl acetic ester, can not (as Collie admitted) be expected to result

[1] *Ber.*, 25, 342 (1892).
[2] *Ibid.*, 25, 432 (1892).
[3] *J. Chem. Soc.*, 47, 277 (1885).

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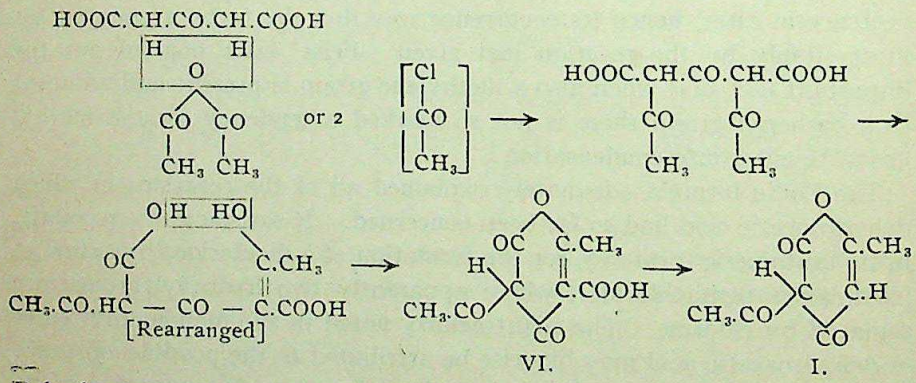
from this manner of condensation. Though the structure of dehydroacetic and dehydrobenzoylacetic acid[1] are no doubt identical, the latter must arise from some other reaction. Collie's formula may be considered as the δ-lactone of hydroxyacrylylacetic acid; or again, and more pointedly emphasized by Collie, the δ-lactone of tetracetic acid. This hypothetical tetracetic acid may be looked upon as the result of condensation between four molecules of acetic acid, $CH_3.CO.CH_2.CO.CH_2.CO.CH_2.COOH$, a supposition quite in keeping with Geuther's first hypothesis of the dehydration of acetic acid alone, hence the name as then proposed.

v. Pechmann,[2] in his studies upon acetonedicarboxylic acid, announced a new method for the preparation of dehydroacetic acid. This method consisted in warming gently a mixture of acetonedicarboxylic acid and acetic anhydride; the product formed is a dehydroacetocarboxylic acid, which when sublimed readily loses carbon dioxide to give dehydroacetic acid itself. v. Pechmann found also that acetyl chloride reacted equally as well upon acetonedicarboxylic acid and yielded the products just mentioned. The classical investigations by v. Pechmann in this field pointed more particularly to the Feist formula for dehydroacetic acid.

In support of Feist's formula v. Pechmann outlined the following series of reactions:



Dehydroacetocarboxylic acid (VI) is formed by loss of water from the hypothetical sym.-diacetylacetonedicarboxylic acid, one-half of which is assumed to exist in the enolic form. The loss of carbon dioxide, as indicated, leads directly to dehydroacetic acid in accordance with the Feist formula. As further substantiation of this reasoning, v. Pechmann tried the action of propionic anhydride upon acetonedicarboxylic acid. The result was a dehydropropionylacetocarboxylic acid (VII) which, by loss of carbon dioxide, readily gave the expected dehydropropionylacetic acid (VIII). By analogy, formula (IX) would represent the structure of dehydrobenzoylacetic acid.

[1] Baeyer and Perkin, *Ber.*, 17, 64 (1884); *Ibid.*, 18, 3726 (1885).
[2] *Ber.*, 24, 3600, 4098 (1891); *Ann.*, 273, 186 (1893).

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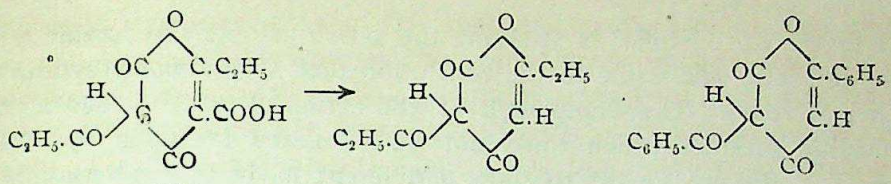
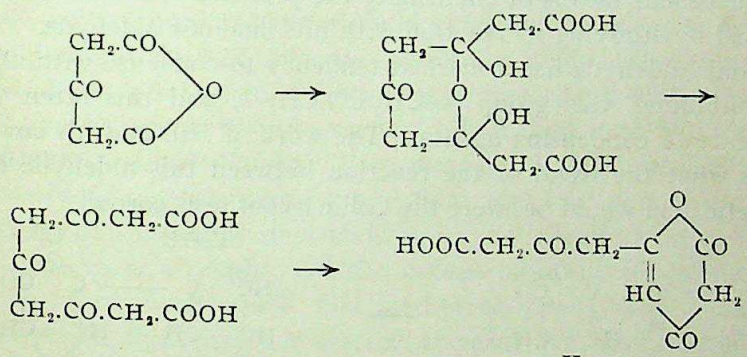


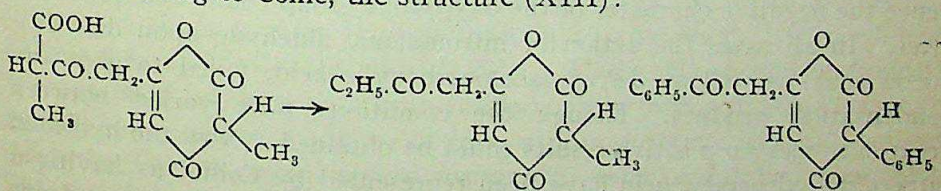
VII. VIII. IX.

If the Collie formula is the correct one then an entirely different mode of condensation must here be considered.[1] Acetonedicarboxylic anhydride is first formed; this in turn reacts with one molecule of acetic anhydride to form a dicarboxylic acid which, upon heating, adds water to open the ring and then passes over into a diacetylacetonedicarboxylic acid; this latter forms at once the lactone or dehydroacetocarboxylic acid (X) and finally by loss of carbon dioxide yields dehydroacetic acid itself (IV):



X.

According to Collie, therefore, the constitution of v. Pechmann's dehydropropionylacetocarboxylic acid must have a similar constitution (XI) to give eventually dehydropropionylacetic acid (XII). And dehydrobenzoylacetic acid, whether or not formed in this manner, should have, according to Collie, the structure (XIII):



XI. XII. XIII.

Since the extensive work of Feist and Collie on this acid, a number of others have contributed much toward its final solution. Dieckmann and Breest[2] showed that the action of acetylchloride upon triacetic lactone need not be construed as an argument against Feist's formula as Collie

[1] *J. Chem. Soc.*, 77, 977 (1900).
[2] *Ber.*, 37, 3387 (1904).

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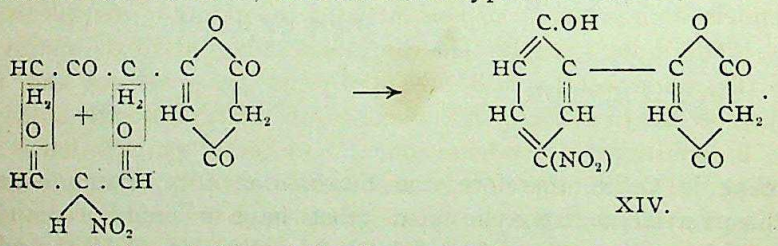
has suggested.[1] Stollé[2] in studying the action of phenylhydrazine upon dehydroacetic acid came to the conclusion that a true phenylhydrazone is here formed. This compound, by the action of acid, yielded a condensation product which could not be accounted for upon the Collie formula. Bülow[3] sought to show a different mode of condensation of this acid with N-amido derivatives and was inclined to accept the Collie formula. The results of Stollé, however, have been confirmed in the past year by E. Benary[4] and the evidence gained through the phenylhydrazine reaction shown to conform with the Feist formula.

There is no doubt therefore but that the formula for dehydroacetic acid rests upon one of these two possible structures, with the more recent evidence favoring somewhat the Feist hypothesis. Granting for the time that the Collie formula may be the correct one, it seemed that we might have an excellent means of confirming the presence of an acetonyl group in this acid by studying its reaction with nitromalonic aldehyde. Sodium nitromalonic aldehyde has a marked tendency to condense with all derivatives containing the group $—CH_2.CO.CH_2—$, and this often without the presence of condensing agents. The work of Hill and his coworkers[5] indicates what the trend of the reaction between this aldehyde and dehydroacetic acid would be, were the Collie hypothesis correct,



XIV.

When one of the substituents in the acetone group is strongly negative, a greater concentration of alkali or condensing agent may be required,[6] hence the negative character of the oxypyrone group could well be looked after. In all cases the action of nitromalonic aldehyde upon dehydroacetic acid, as well as dehydroacetocarboxylic acid, failed to give any condensation product. Though the conditions were varied between great extremes no positive results could be obtained. Now the hydrated salts of dehydroacetic acid have been represented by Collie[7] as having a formula such as $CH_3.CO.CH_2.CO.CH_2.CO.CH_2.COONa$, and by loss of one molecule of water passing over into that type as given by Collie for dehydro-

[1] *J. Chem. Soc.*, 59, 607, 617 (1891); *Ibid.*, 77, 976 (1900).
[2] *Ber.*, 38, 3026 (1905).
[3] *Ibid.*, 41, 4161 (1908).
[4] *Ibid.*, 43, 1070 (1910).
[5] *Am. Chem. Jour.*, 22, 89 (1899); *Ibid.*, 24, 1 (1900); *Ibid.*, 33, 1 (1905).
[6] Hale and Robertson, *Am. Chem. Jour.*, 39, 680 (1908).
[7] *J. Chem. Soc.*, 77, 974 (1900).

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acetic acid in its enolic form (V). Such an arrangement of acetonyl groups, as thus pictured by Collie, would offer several possibilities for a ready condensation with nitromalonic aldehyde; but, as just stated, the absence of any condensation whatsoever with this most reactive substance points conclusively to the non-existence of the nucleus, $—CH_2.CO.CH_2—$, or the tautomeric form with which it may be in equilibrium; the presence of the latter is found not to interfere with the final result in these condensations. Similarly the action of nitromalonic aldehyde upon dehydrobenzoylacetic acid, as well as dehydropropionylacetic acid, netted no positive results. Upon this purely negative evidence we are inclined to accept the Feist formula as the correct one and have applied further tests to confirm this conclusion.

The action of benzaldehyde, for example, was studied with a view of determining the possible condensation under the influence of acid or alkali. From the observations of Goldschmiedt,[1] Harries and others[2] it has been pointed out that aromatic aldehydes react with saturated unsymmetrical ketones in two different ways: preferably with the methyl group of the ketone in the presence of alkali, and with the methylene group in the presence of acid. Stoermer and Wehln[3] further showed, from a study of phenoxylacetone and benzaldehyde, that the course of this condensation is largely dependent upon the nature of the substituent groups. The more strongly acid the radicle adjacent to the methylene group, the more reactive will this methylene group become and, as a consequence, the more likely it is alone to react with aromatic aldehydes under all conditions of condensation, *i. e.*, whether the solution is acid or alkaline. The example of acetoacetic ester, with its strongly negative carbethoxyl adjacent to the methylene group, in giving only the compound benzylidene acetoacetic ester,[4] $CH_3.CO.C : (CHC_6H_5).COOC_2H_5$, under the influence of alkali as well as acid is thus well accounted for. Phenoxylacetone, $C_6H_5O.CH_2.CO.CH_3$, condenses with one molecule of benzaldehyde in either acid or alkaline solution to give only the benzylidene phenacetol, $C_6H_5O.C(:CHC_6H_5).CO.CH_3$. When this methylene group is once involved, the remaining methyl group may, in some cases of which this is one, be made to combine with a second molecule of benzaldehyde. The analogy between acetoacetic ester and phenoxylacetone lies, therefore, in the negative character of the carbethoxyl and phenoxyl groups; the latter, however, is not so negative as the former and yet much more so than the phenyl group, as just cited in the studies of Goldschmiedt.

[1] *Monatsh.*, 18, 437 (1897); 19, 461 (1898); 22, 659 (1901).
[2] *Ber.*, 35, 966 (1902); *Ibid.*, 35, 3088 (1902).
[3] *Ibid.*, 35, 3549 (1902).
[4] *Ibid.*, 14, 347 (1881); *Ibid.*, 29, 172 (1896); *Ann.*, 218, 177 (1883); *Ibid.*, 281, 63 (1894).

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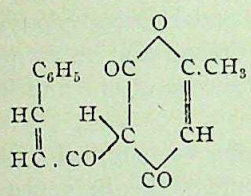
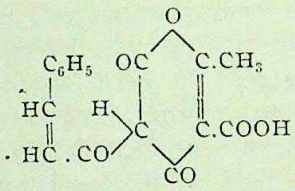
If we now look upon the formulas assigned to dehydroacetic and dehydroacetocarboxylic acids by Collie on the one hand, and by Feist upon the other, we may draw certain conclusions which these studies with benzaldehyde should lead us to expect. Since benzaldehyde has a tendency to condense with a methylene or methyl group only when adjacent to a carbonyl group, Feist's formula for these acids could give for each only one possible product: benzylidene dehydroacetic acid (XV) and benzylidene dehydroacetocarboxylic acid (XVI):



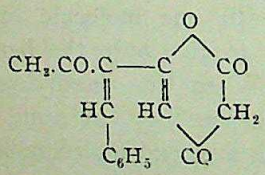
XV.



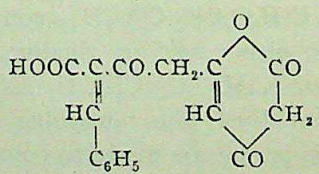
XVI.

These condensations should proceed easily when the aldehyde and the acid are brought together in alkaline solution. The work of Harries and others has indicated the trend of just such a condensation when a methyl group is present. The absence of a methylene group may be expected to make possible any condensation with a methyl group when the solution is alkaline, and again it must reduce to a minimum any chance for this methyl group to enter into condensation when the solution is acid.

In the consideration of Collie's formulas for these two acids the acetonyl group, as the side chain, would offer only two possibilities. For dehydroacetic acid we probably should have only one molecule of benzaldehyde entering into reaction in the acetone nucleus, and this with the methylene group alone, owing to the acid character of the pyronone ring as the substituent (XVII). This condensation, however, should proceed in acid solution, whereas in alkaline solution the same end result would



XVII.



XVIII.

be obtained. It is doubtful whether or not the methyl group of this side chain could be made to enter into condensation. If possible it would react in alkaline solution. Now in addition to this acetone nucleus there is a methylene group in the pyronone ring and here, as elsewhere, the tendency would naturally be for benzaldehyde to condense easily in acid solution (if not also in alkaline solution).

For dehydroacetocarboxylic acid Collie accounts for the carboxyl on the end of the acetonyl chain. In other words he reproduces the

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exact conditions that are present in acetoacetic ester, where a methylene group is adjacent to a strongly negative or acid group. The tendency therefore must be that benzaldehyde will condense most readily with this particular methylene group in acid solution. In alkaline solution, also, the same product should result (XVIII). Whether the second methylene group, adjacent to the ring, or the methylene group in the ring is also involved need not concern us; the conditions, however, certainly favor the condensation with a second molecule of benzaldehyde.

The facts are that dehydroacetic acid, as well as dehydroacetocarboxylic acid, condenses with only one molecule of benzaldehyde in alkaline solution. In acid solution dehydroacetocarboxylic acid refuses altogether to condense with this aromatic aldehyde and dehydroacetic acid, if at all, condenses with benzaldehyde in acid solution in only the very smallest degree. This absence of condensation in acid solution forces us to the conclusion that in dehydroacetocarboxylic acid there can not possibly be a methylene group adjacent to a carboxyl as is demanded by the Collie formula. The analogy with acetoacetic acid breaks down completely in this instance. Again in dehydroacetic acid itself the absence of any condensation product in acid solution, other than a small amount of the same product as is obtained in alkaline solution, shows that the methylene groups as here demanded by the Collie formula are entirely without activity—a supposition hardly warranted by the exhaustive and careful studies of Harries and others upon the ease with which aromatic aldehydes enter into condensation with these groups.

According to the formula assigned to dehydrobenzoylacetic acid in accordance with the Feist hypothesis (IX) a condensation of this acid with benzaldehyde would not be possible, a conclusion substantiated by the experimental results, whereas according to the Collie formula for this acid (XIII) we have just that condition which should be most favorable for condensation of methylene groups with benzaldehyde, especially in acid solution. Herein is further proof that Feist's form la alone stands in full agreement with the facts observed.

In order now to attack the problem from the constructive point of view it was thought best to try out v. Pechmann's hypothesis and ascertain, if possible, the exact course of the reaction between acetic anhydride and acetonedicarboxylic acid. If this reaction proceeds in the manner outlined by v. Pechmann and all chances for a condensation in accordance with the plan outlined by Collie, to yield an acid of the structure he proposed, were eliminated, then it would appear that a most conclusive proof of the Feist formula is at hand.

When benzoic anhydride is made to replace acetic anhydride in the v. Pechmann reaction a beautifully crystalline product is obtained. This may be prepared also by the action of benzoyl chloride in place of the

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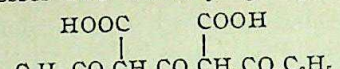
anhydride. The product is a symmetrical dibenzoylacetonedicarboxylic acid (XIX). It possesses two carboxyl groups and four ionizable hy-



XIX.

drogen atoms. Unfortunately the compound undergoes decomposition upon heating (even before melting) and can not be made to pass over into a dehydrobenzoylacetocarboxylic acid (analogy with the hypothetical diacetylacetonedicarboxylic acid, see (VI)) as was expected. For this result, of course, a partial tautomerization into the enolic form would be a prerequisite, and were it possible to heat the compound for any length of time without complete decomposition, such a result may well be anticipated.

The action of dry hydrogen chloride upon this product dissolved in absolute alcohol gives the diethyl ester. This ester is acid in character with two ionizable hydrogen atoms. There can be no doubt as regards the structure of either the acid or its diethyl ester. Even by gentle heating the ester also undergoes ready decomposition and shows no tendency to condense into a dehydrobenzoylacetocarboxylic acid, as might be inferred from the action of heat upon benzoylacetic ester. A warm barium hydroxide solution hydrolyzes the ester, or the acid, into the constituents—benzoic acid and free acetonedicarboxylic acid. With too strong acid or alkali complete decomposition ensues.

By the use of benzoacetic anhydride in place of benzoic anhydride it was thought possible to favor this partial tautomerization, through the presence of one acetyl group, if such takes place as described in the case of acetic anhydride itself when acting upon acetonedicarboxylic acid. The product, however, is so extremely unstable that no positive results as yet have been obtainable.

Various means were then brought to bear upon the dibenzoylacetonedicarboxylic acid with the hope of effecting some partial condensation, at least, within its molecule, but in no case was such a result accomplished. Quite unexpectedly it was found that the action of acetic anhydride upon this dibenzoylacetonedicarboxylic acid yielded the dehydroacetocarboxylic acid of v. Pechmann. A long boiling is necessary when the anhydride alone is employed, but with the addition of a drop or two of conc. sulfuric acid the action is complete in a very few minutes. The diethyl ester does not react with acetic anhydride. We have, therefore, in this reaction a key to the mechanism of the reaction of acetic anhydride upon acetonedicarboxylic acid. Just as the benzoyl groups attach themselves to the acetone nucleus so also must the acetyl groups arrange themselves in this same molecule—one acyl group replacing a hydrogen atom in each of the two methylene groups. In considering

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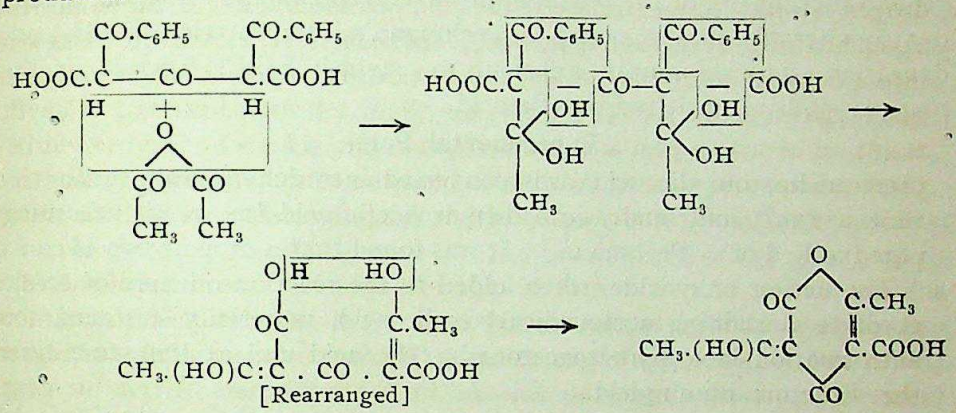
the action of acetic anhydride upon the dibenzoyl derivative we may construe it as a repetition of the symmetrical condensation in which now the two single hydrogen atoms of the methine groups are replaced by acetyl and then, through addition of water and conversion into the enolic form, benzoic acid is split off and dehydroacetocarboxylic acid at once produced:



[Rearranged]

More simply, perhaps, we may look upon the action as merely one of replacement of benzoyl by acetyl groups and final condensation of the exceedingly unstable diacetyl derivative into its δ-lactone or dehydroacetocarboxylic acid. The slowness of this action in the presence of acetic anhydride alone confirms the belief that the acetyl groups must eventually supplant the benzoyl groups.

Though the dibenzoylacetonedicarboxylic acid could not be raised to a temperature at which tautomerization and finally intramolecular condensation was possible, this replacement of the two benzoyl groups, of known position, by acetyl groups, just prior to their entering into the tautomeric form and final condensation of the molecule into dihydroacetocarboxylic acid, offers conclusive proof on the conditions which underlie the v. Pechmann reaction. As still further proof, in substantiation of this explanation, the action of propionic anhydride upon dibenzoylacetonedicarboxylic acid is found to give most readily the corresponding dehydropropionylacetocarboxylic acid (VII) of v. Pechmann m. 114–5°.[1]

According to the plan outlined by Collie (see above) there can be no possible condensation of benzoylchloride, or benzoic anhydride, with acetonedicarboxylic acid. In fact the only chance for benzoic anhydride to enter here into condensation, leaving the two carboxyl groups free, is in accordance with Feist's hypothesis. We may assume then once for all that it is the halogen of benzoyl chloride, or the anhydride oxygen of benzoic anhydride, that actually enters directly into reaction with the acetone nucleus. The compound formed is exceedingly unstable

[1] *Ann.*, 273, 201 (1893).

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when one or two acetyl groups constitute the entering factors, passing over in the latter case into its δ-lactone, a derivative of dehydroacetic acid.

Investigations upon other anhydrides in this connection have been undertaken, particularly the study of phenylacetic anhydride. The general mechanism of the reaction, however, remains the same and stands out conclusively in support of v. Pechmann's interpretation of this condensation—a proof amply sufficient to estabish Feist's formula as the only possibility for dehydroacetic acid.

Experimental Part.

Acetonedicarboxylic acid[1] was converted into dehydroacetocarboxylic acid (m. 154°) and finally into dehydroacetic acid (m. 109°) according to the method of v. Pechmann.[2] It was found that a drop or two of conc. sulfuric acid or anhydride, when added to the reaction mixture of acetic anhydride containing acetonedicarboxylic acid, materially hastened the transformation into dehydroacetocarboxylic acid and at the same time insured the maximum yield.

Attempts at Condensation with Sodium Nitromalonic Aldehyde.—If Collie's hypothesis is the correct one, then the condensation with nitromalonic aldehyde should proceed with great ease and a product of the constitution as shown in formula (XIV) would be produced. This substance, if formed, would give by oxidation the well-known *m*-nitro-*o*-hydroxybenzoic acid. Solutions of dehydroacetic acid containing from one to ten molecules of sodium hydroxide, $N/10$ solution, were allowed to stand a number of days with sodium nitromalonic aldehyde in equimolecular quantities. A slight red coloration usually made its appearance, but in all cases upon acidification the original weight of dehydroacetic acid was recovered. Piperidine, diethylamine, and other condensation agents were employed but always with negative results. In a similar manner, only negative results were obtained from attempts to condense dehydroacetocarboxylic acid with nitromalonic aldehyde.

Benzylidene Dehydroacetocarboxylic acid, $C_{16}H_{12}O_6$ (XVI).—Two grams of dehydroacetocarboxylic acid were dissolved in 50 cc. of water and 7 cc. of 2 N sodium hydroxide solution added to alkaline reaction. Two grams of freshly distilled benzaldehyde were then admitted and the flask set in a shaker for two or three days. The contents of the flask were then extracted with ether to remove the excess of benzaldehyde and the aqueous solution acidified with hydrochloric acid, upon which the lemon-yellow benzylidene was precipitated. The weight of the dry product was 2.2 grams. Benzylidene dehydroacetocarboxylic acid is insoluble in water; only slightly soluble in ether, but readily soluble in chloroform, benzene,

[1] *Ann.*, 261, 155 (1891).

[2] *Ber.*, 24, 3600 (1890); *Ann.*, 273, 186 (1893).

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acetic ester, or acetone. It is fairly soluble in hot ligroin, crystallizing out on cooling, and quite soluble in hot alcohol from which it crystallizes best in the form of needle clusters. The product melts at 147–8° (cor.). Upon sublimation, twice or three times repeated, it gives dehydroacetic acid m. 109°.

The action of benzaldehyde upon dehydroacetocarboxylic acid in acid solution failed to give either this benzylidene or any other condensation product. The dehydroacetocarboxylic acid was dissolved in benzaldehyde and treated with dry hydrogen chloride in the cold and the mixture allowed to stand a week or more. Again the acid was dissolved in chloroform, and also in benzene, and into each of these solutions containing benzaldehyde in excess, the introduction of dry hydrogen chloride was unproductive of results. In all cases the unacted-upon dehydroacetocarboxylic acid was recovered.

In the crystallization of the benzylidene compound from alcohol considerable care must be used, as slight traces of alkali that may still be present work toward its rapid decomposition in alcoholic solution.

Calculated for $C_{16}H_{12}O_6$: C, 63.98; H, 4.03.
Found: C, 63.71; H, 4.31.

Benzylidene Dehydroacetic Acid, $C_{15}H_{12}O_4$ (XV).—Into a solution containing 2 grams of dehydroacetic acid in 80 cc. of water 6 cc. of 2 *N* sodium hydroxide solution were added to alkaline reaction. Two grams of freshly distilled benzaldehyde were then admitted to the flask and the latter set in a shaker for two or three days. The contents of the flask were then extracted with ether to remove free benzaldehyde and the aqueous residue acidified, whereupon the light yellow benzylidene compound was precipitated. Benzylidene dehydroacetic acid is extremely soluble in benzene, alcohol, acetic ester, chloroform, acetone, or ether. It is fairly soluble in hot ligroin, from which it separates in poorly defined crystals, and fairly soluble in hot water, crystallizing best from this solution in irregular needle clusters, almost colorless and melting at 105–6° (cor.). By sublimation this benzylidene compound passes back readily into dehydroacetic acid.

Calculated for $C_{15}H_{12}O_4$: C, 70.30; H, 4.68.
Found: C, 70.12; H, 4.91.

The action of dry hydrogen chloride upon a mixture of benzaldehyde and dehydroacetic acid in a cold chloroform solution was unproductive of results. When dehydroacetic acid is dissolved in the benzaldehyde and a current of dry hydrogen chloride led through the reaction mixture a slight change is noted. If this mixture, after standing several days, is neutralized with sodium hydroxide solution and all excess of benzaldehyde removed by shaking with ether, the addition of hydrochloric acid will precipitate a slightly yellow colored compound which

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consists of a mixture of dehydroacetic acid and the benzylidene derivative of this acid just described. It is probable that the alkali added above may have facilitated the formation of this product, and again it is not unlikely that the pyronone group of dehydroacetic acid is sufficiently acid to interfere in any appreciable way with the formation of the regular benzylidene compound described above, even in acid solution.

s-Dibenzoylacetonedicarboxylic Acid, $C_{19}H_{14}O_7$ (XIX). — The crude acetonedicarboxylic acid obtained by the method of v. Pechmann[1] and still somewhat moist with sulfuric acid may advantageously be used in this work. A flask containing 32 grams of benzoic anhydride is set upon a steam bath and into the molten anhydride 4 grams of acetonedicarboxylic acid are added with vigorous stirring. Solution takes place rapidly, but no less benzoic anhydride than eight times the weight of acetonedicarboxylic acid will serve for a clear solution. The color of the reaction-mixture becomes at first a yellow but passes into a dark red in a very few minutes. Considerable heat is given out by the reaction itself. After 2 or 3 minutes the action is at an end. A little ether is now added to the flask (care being taken to keep flask closed during this step to avoid loss) until the reaction-mixture is increased to twice its original volume and the contents of the flask appear as a homogeneous mixture. Into the flask, with its contents still warm, an excess of ether (equal in volume to that of the total reaction-mixture) is now poured when as a result a yellow semi-crystalline substance will be precipitated. The contents of the flask are now poured out upon a suction filter and the precipitate washed with warm ether. The ether serves to remove the large excess of benzoic anhydride and acid. From the ether mother liquors a considerable quantity of benzoic anhydride may be recovered. The precipitate, however, still contains a small amount of these impurities. Its purification is easily effected by solution in hot benzene from which the almost pure dibenzoylacetonedicarboxylic acid separates immediately. From the benzene mother liquor, evaporated to dryness and washed with ether, a small quantity of the dibenzoyl derivative may be procured. From the 4 grams of crude acetonedicarboxylic acid 1.9 grams of the pure product were obtained.

In place of benzoic anhydride somewhat less of benzoyl chloride will suffice for this same reaction. The operation is carried out in an exactly analogous manner, but much more disagreeably to the operator.

s-Dibenzoylacetonedicarboxylic acid is insoluble in water, ligroin, carbon tetrachloride or ether; soluble in cold acetone or acetic ester; and fairly soluble in hot chloroform, glacial acetic acid, alcohol or benzene, crystallizing from each upon cooling, but more easily from the last named.

[1] *Loc. cit.*

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It appears in the form of colorless leaflets when pure, melting at 162° (cor.) with decomposition slightly below this point.

Calculated for $C_{19}H_{14}O_7$: C, 64.39; H, 3.98.
Found: C, 64.43; H, 4.23.

When titrated 0.0930 gram substance required 10.2 cc. $N/10$ NaOH solution. Calculated for 4 molecules of NaOH 10.5 cc. should have been used. Hence the presence of 4 ionizable hydrogen atoms. From these neutral and very dilute solutions, hydrochloric acid will reprecipitate the dibenzoyl derivative unchanged. Mild alkalies easily saponify this compound, giving benzoic acid and acetonedicarboxylic acid.

When this dibenzoylacetonedicarboxylic acid is subjected to heat, carbon dioxide is evolved at a very early stage and benzoic acid sublimes from the molten mass shortly afterwards. When the compound is dissolved in acetic anhydride and then submitted to heat no apparent action takes place, but if the solution is boiled a change of color is noticed and the benzoyl groups are gradually replaced by the acetyl groups with the subsequent formation of dehydroacetocarboxylic acid. This end is brought about almost immediately if a few drops of concentrated sulfuric acid are added to the acetic anhydride solution and the mixture warmed upon the steam bath. When the deep red color is developed (after 4 or 5 minutes) water is gradually added to the mixture and the yellow glistening flakes of dehydroacetocarboxylic acid (m. 154°) of v. Pechmann appear. There can be no doubt but that the acetyl actually replaced the benzoyl groups. The mother liquor showed the presence of benzoic acid as was expected.

From attempts at heating dibenzoylacetonedicarboxylic acid in molten benzoic anhydride with a view to making possible the condensation into dehydrobenzoylacetocarboxylic acid, without this tendency for replacement of the benzoyl groups present, no definit results have been obtained. Decomposition, of course, set in early with an evolution of carbon dioxide. Dry hydrogen chloride was without action upon this dibenzoyl derivative dissolved in benzene as well as in other anhydrous solvents.

If dibenzoylacetonedicarboxylic acid is dissolved in propionic anhydride and the solution, after the addition of a drop of sulfuric acid, warmed upon a steam bath, the complete replacement of the benzoyl by propionyl groups is effected. The product obtained by dilution of the reaction-mixture is the crystalline dehydropropionylacetocarboxylic acid of v. Pechmann, melting at 114–5°.

Diethyl Ester of s-Dibenzoylacetonedicarboxylic Acid, $C_{23}H_{22}O_7$ (see XIX).—A stream of dry hydrogen chloride is passed into a flask, set in freezing mixture, and containing 3 grams of dibenzoylacetonedicarboxylic acid suspended in 8 or 9 times its weight of absolute alcohol. When complete saturation is reached and solution effected, the flask is corked

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and set aside in cool place over night. The clear red solution is then poured into a beaker containing cracked ice, and after an hour or more the needle-like crystals filtered off and dried upon a porous plate. The mother liquor should be extracted with ether several times and the ether solutions evaporated to small bulk, dried with calcium chloride, and then freed of ether by warming over a steam bath. When cool the introduction of a crystal of the crude product, as filtered off above, will usually start crystallization. The entire crystalline mass dried upon a porous plate weighed 1.8 grams. When dissolved in benzene with the addition of a small quantity of ligroin there soon appeared beautiful long needles of the pure, colorless diethyl ester m. 70.5° (cor.). This diethyl ester is almost insoluble in water but extremely soluble in acetic acid, acetone, alcohol, chloroform, acetic ester or benzene; it is fairly soluble in hot ligroin, from which it crystallizes in needle clusters upon cooling. The best means of purification consists in dissolving the ester in a small quantity of benzene and adding ligroin to this clear solution; almost immediately the large needle clusters appear.

Calculated for $C_{23}H_{22}O_7$: C, 67.28; H, 5.40.
Found: C, 67.20; H, 5.67.

In a molecular weight determination in benzene solution,

I. 0.1754 gram substance in 17.40 grams benzene caused a depression of 0.116° in the freezing point of solvent.

II. 0.2593 gram substance in 17.40 grams benzene caused a depression of 0.170° in the freezing point of solvent.

Calculated for $C_{23}H_{22}O_7$: Mol. wt., 410.16; Found: I, 417.1 and II, 420.8.

For titration with N/10 sodium hydroxide solution (phenolphthalein as indicator). 0.1230 gram substance required 6.2 cc. of this alkaline solution. Calculated for 2 molecules of NaOH, 6 cc. should have been used. Hence the presence of two ionizable hydrogen atoms is shown.

This diethyl ester is in fact quite acid in its reactions, as may be inferred at once from the position of the hydrogen atoms on the carbon atoms adjacent to these carbonyl groups. From its dilute neutral solutions hydrochloric acid will reprecipitate the ester unchanged.

By the application of heat the ester, after melting, undergoes ready decomposition with the liberation of benzoic acid. No condensation product was detected in the charred mass.

Acetic anhydride is without action upon this ester just as v. Pechmann reported true for the diethyl ester of acetonedicarboxylic acid.

When boiled with a barium hydroxide solution the diethyl ester is readily saponified. After the hot mixture is filtered, acidification of the filtrate and extraction with ether gave crystals of benzoic acid. From the precipitate, taken up in hydrochloric acid and extracted with ether, was obtained the white crystals of the original acetonedicarboxylic acid, m. 135°.

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The Action of Benzoacetic Anhydride upon Acetonedicarboxylic Acid.—This anhydride was prepared to the method of Gerhardt[1] but is difficult to obtain in a high degree of purity. When acetonedicarboxylic acid is dissolved in this anhydride, warmed upon a steam bath, immediate action ensues. After a few minutes the red colored product was mixed with ether in excess and the undissolved portion filtered off. This precipitate, however, can not be dried, owing to its great tendency for decomposition. It may be preserved under ether for a short time. Several attempts were made to bring about a condensation in its molecule—supposedly a benzoylacetylacetonedicarboxylic acid—to form a benzoyl methylpyronone derivative of similar structure to dehydroacetic acid. No positive results, however, were obtained, and owing to the difficulty in securing what may be called the pure benzoacetic anhydride, no further work was attempted in this direction.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE FORMATION OF BENZALDEHYDE AND 2,4,6-TRIBROMOANILINE FROM 3,5-DIBROMO-4-AMINOBENZHYDROL BY THE ACTION OF BROMINE.

BY LATHAM CLARKE AND GUSTAVUS J. ESSELEN, JR.

Received May 8, 1911.

While engaged on the study of certain bromine derivatives of 4-aminobenzophenone and 4-aminobenzhydrol, the following experiment was performed.

Five grams of 4-aminobenzhydrol (prepared by reducing 4-aminobenzophenone with sodium amalgam in alcoholic solution)[2] were dissolved in 150 cc. of washed and dried chloroform and to the solution 4 grams (two atoms) of bromine were added. A precipitate was thrown down and soon clotted together to form what appeared under a magnifying glass as a mixture of yellowish crystals and a yellow tarry mass. This precipitate was filtered off but could not be made to yield a crystalline substance—water, ether, acetone, naphtha, benzene, ethyl alcohol, chloroform, glacial acetic acid and ethylene dibromide were tried in vain. The material was soluble in alcohol and when the latter was evaporated off, a dark yellow jelly remained which had the odor of benzaldehyde. No pure products could be obtained, but this was probably due to the presence of an anhydride of high molecular weight, identical with or analogous to that described by Kippenberg,[3] and formed from 4-aminobenzhydrol by the action of hydrobromic acid. In our case hydro-

[1] *Ann.*, 87, 81 (1853).
[2] Kippenberg, *Ber.*, 30, 1135.
[3] *Ibid.*, 30, 1137, 1138.

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bromic acid was produced and liberated in small amounts on adding the bromine to the solution of the 4-aminobenzhydrol.

Subsequent experiments always gave a noticeable odor of benzaldehyde when the solvent was evaporated, but on account of the unmanageable nature of the reaction product benzaldehyde could not be isolated.

It seemed, however, as if a side reaction had taken place whereby the benzaldehyde had been formed by a splitting of the 4-aminobenzhydrol in the following manner,

$$C_6H_4—CH(OH)—C_6H_4NH_2 + Br_2 = C_6H_5—CHO + HBr + BrC_6H_4NH_2,$$

giving benzaldehyde, para bromaniline and hydrobromic acid. We had evidence of benzaldehyde and hydrobromic acid, but could detect no *p*-bromoaniline.

In order to ascertain whether such a reaction would take place in other cases or not, we decided to prepare 2,5-dibromo-4-aminobenzhydrol and to treat this with bromine. In this case the presence of the two atoms of bromine would probably prevent the formation of a compound analogous to Kippenberg's anhydride, and unhampered by this reaction we should be able to study the action of the bromine on the hydrol grouping, if such took place.

We therefore synthesized 2,5-dibromo-4-aminobenzhydrol by preparing first, 4-aminobenzophenone; treating this with four atoms of bromine gave 2,5-dibromo-4-aminobenzophenone,[1] and this when reduced with aluminum amalgam yielded the desired 2,5-dibromo-4-aminobenzhydrol. Summarizing these reactions:

$C_6H_5.CO.C_6H_4NH_2$, *p*-aminobenzophenone

$C_6H_5.CO.C_6H_2Br_2NH_2$, 3,5-dibromo-4-aminobenzophene

$C_6H_5CH(OH)C_6H_2Br_2NH_2$, 3,5-dibromo-4-aminobenzhydrol.

3,5-Dibromo-4-aminobenzhydrol was then treated in chloroform solution with two atoms of bromine, and thereby were produced, benzaldehyde, 2,4,6-tribromoaniline and hydrobromic acid. No other compounds were formed sufficient in amount to be detected. The benzaldehyde was identified in addition to its ordinary properties by conversion into the phenylhydrazone. From the original reaction mixture by passing into the solution dry gaseous hydrogen chloride, the 2,4,6-tribromoaniline was precipitated in the form of the hydrochloride, which on recrystallization from alcohol gave up its hydrochloric acid and the free 2,4,6-tribromoaniline was then identified by its physical properties and analysis.

This reaction between bromine and 3,5-dibromo-4-aminobenzhydrol may be expressed in this way:

$$\underset{\ \ Br\ \ Br}{C_6H_5—CH(OH)—C_6H_2Br_2NH_2} \longrightarrow C_6H_5CHO + C_6H_2Br_3NH_2 + HBr.$$

[1] The proof of the positions of these two atoms of bromine is given later in this paper.

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The mechanism of the reaction may be that the hydrol is first split into tribromaniline and bromphenylhydroxymethane which last breaks down into benzaldehyde and hydrobromic acid, thus:

$$C_6H_5CH(OH)Br + C_6H_2Br_3NH_2 \longrightarrow C_6H_5CH:O + HBr$$

The fact that tribromoaniline is obtained, with bromine atoms arranged on each side of the NH_2 group, proves the bromine atoms in the original dibromo-4-aminobenzhydrol to have been in the 3,5-positions.

We shall study the reaction further and shall extend our investigations to other derivatives of benzhydrol, to see if this reaction is a general one.

Experimental Part.

Preparation of p-Aminobenzophenone.—The first of the *p*-aminobenzophenone used in this work was made by the following process: Phenylbenzoylamide was formed by heating together aniline and benzoyl chloride according to the method of Gerhardt.[1] This has the formula

$$C_6H_5—NH—COC_6H_5.$$

On heating with benzoyl chloride and anhydrous zinc chloride this formed benzoyl-*p*-aminobenzophenone,[2]

$$C_6H_5—CO—C_6H_4NH—CO—C_6H_5.$$

By boiling the last with alcoholic soda, it was saponified, giving *p*-aminobenzophenone and sodium benzoate.

In the later work a new method has been devised for the preparation of *p*-aminobenzophenone, which was suggested by the work of Chattaway,[3] who showed that when dibenzanilide was heated with anhydrous zinc chloride at 220–230° for twenty hours, a rearrangement took place, *viz.*,

$$C_6H_5N\begin{matrix}\diagup COC_6H_5 \\ \diagdown COC_6H_5\end{matrix} \longrightarrow C_6H_5COC_6H_4\overset{(4)}{N}HCOC_6H_5 \text{ and } C_6H_5COC_6H_4\overset{(2)}{N}HCOC_6H_5.$$

The scheme in brief for this new method of preparing *p*-aminobenzophenone consists in first allowing two molecules of benzoyl chloride to act on one molecule of aniline at 170–180° for a few moments, forming benzanilide together with a small amount of dibenzanilide, then, by the addition of anhydrous zinc chloride and the raising of the temperature to 200°, the remaining benzoyl chloride tends to substitute in the ring rather than in the amino group and whatever dibenzanilide has been already formed will tend to rearrange as indicated by Chattaway,[4] giving benzoyl *p*-aminobenzophenone which can then be saponified.

This was actually carried out in the manner of the following experiment;

[1] *Ann.*, 60, 31.
[2] Higgin, *J. Chem. Soc.*, 41, 133.
[3] *J. Chem. Soc.*, 85, 394.
[4] *Loc. cit.*

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To 100 grams of aniline contained in a two-liter flask, fitted with an air condenser, 330 grams (a slight excess above two molecules) of benzoyl chloride were slowly added from a dropping funnel, and the mixture heated in an oil bath for fifteen minutes at 170–180°, when 5 grams of pulverized, anhydrous zinc chloride were introduced and at the same time the temperature was increased to 200–210°. The oil bath was maintained at this temperature for ten hours, while every two hours 3 grams of pulverized anhydrous zinc chloride were added. At the end of this time the hot liquid was poured out into an enameled iron dish, where it cooled and solidified and was later recrystallized from alcohol. This process ran very smoothly and the reaction mixture was practically free from charring. After twice recrystallizing from alcohol, the benzoyl *p*-aminobenzophenone was white and ready for saponification. The yield was in various experiments from 85–90 grams.

In saponifying the benzoyl *p*-aminobenzophenone the method of Döbner[1] was used, namely, boiling with alcoholic soda. For every 10 grams of benzoyl *p*-aminobenzophenone 2 grams of ordinary sodium hydroxide were used. The sodium hydroxide was dissolved in 12.5 cc. of water and added to the benzoyl-*p*-aminobenzophenone dissolved in 43 cc. of hot alcohol. The solution was refluxed on a steam bath for seven hours, and water added hot, just to turbidity. On cooling, *p*-aminobenzophenone separated out in feathery crystals and was purified either by crystallizing from carbon tetrachloride or by dissolving in hot alcohol and adding hot water just to turbidity and allowing to cool. The yield was 90–95 per cent. of the theoretical.

3,5-Dibromo-4-aminobenzophenone.—For the preparation of this compound in a typical experiment 10 grams of *p*-aminobenzophenone were dissolved in 100 cc. of dry chloroform (which had been washed three times with distilled water and dried carefully with calcium chloride) and to the solution four atoms—that is, 16.2 grams—of bromine were added, and the whole heated with a return condenser for two hours. During the boiling, hydrobromic acid vapors were given off, but at the end of two hours the evolution of these had ceased, and a perfectly clear solution had resulted. The chloroform was evaporated on the steam bath and left a dark colored, crystalline residue which recrystallized readily from alcohol or glacial acetic acid, and less satisfactorily from much naphtha or a little chloroform. It was actually recrystallized once from alcohol, once from naphtha and six times from alcohol, and was then in the form of fine white needles, melting at 146°.

Calculated for $C_{13}H_9ONBr_2$: Br, 45.05; found, 45.04.

Properties: When recrystallized from alcohol, fine white needles. From naphtha, when allowed to crystallize slowly, long, flat, narrow

[1] *Ann.*, 210, 271.

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plates. Melting point, 146°. It is soluble in acetone, benzene, hot alcohol, chloroform, hot glacial acetic acid, and carbon tetrachloride. Insoluble in water and practically so in cold naphtha. Concentrated hydrochloric acid in a sealed tube at 105–110° for five hours is without action.

3,5-Dibromo-4-aminobenzhydrol.—This was produced from 3,5-dibromo-4-aminobenzophenone by reduction with aluminum amalgam—sodium amalgam having been found to remove the halogen from the ring.

The benzophenone was dissolved in a mixture of 30 parts by weight of hot alcohol and 10 of hot water and to the solution the aluminum amalgam from roughly 20 grams of aluminum were added and the whole heated on the steam bath. At the end of an hour and a half, the hot liquid was decanted from the mercury, filtered from the aluminum hydroxide, and cooled, when white needles precipitated, which were removed by filtration and pressed out on a porous plate. The needles were recrystallized, twice from chloroform and three times from alcohol, until the constant melting point, 147.5°, was reached.

Calculated for $C_{13}H_{11}ONBr_2$: Br, 44.79; found, 44.72.

Properties: This substance crystallizes in white needles, melting at 147.5°. It is soluble in ether, acetone and much naphtha. Soluble also in hot benzene, hot carbon tetrachloride and hot glacial acetic acid. Insoluble in water.

Action of Bromine on 3,5-Dibrom-4-aminobenzhydrol.—For the purpose of examining the action of bromine on the 3,5-dibromo-4-aminobenzhydrol, the latter substance was dissolved in twenty parts by weight of dry chloroform (which had been (previous to drying) thoroughly washed out with water) by warming on the steam bath. A slight excess over two atoms of bromine was then added. The bromine color very soon disappeared, whereupon the solution was cooled quickly down to room temperature and dry hydrochloric acid gas passed in. A yellowish crystalline precipitate formed and was quickly filtered off. The chloroform filtrate was evaporated, leaving a residual oil which had the odor and characteristics of benzaldehyde, but since the quantity was not large, a boiling point was not taken but, instead, it was converted into its hydrazone by dissolving in ether and adding a sufficient quantity of freshly distilled phenylhydrazine. The white precipitate thus produced was crystallized from alcohol, and then melted at 153.5–154°, thus corresponding to the phenylhydrazone of benzaldehyde, the melting point of which is given by Behrend and Leuchs,[1] as 156°. The other properties of our compound were coincident with those of the phenylhydrazone of benzaldehyde.

The yellow crystalline precipitate mentioned above as thrown down from the chloroform solution when dry hydrogen chloride was passed in was

[1] *Ann.*, 257, 227.

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the hydrochloride of 2,4,6-tribromoaniline. It was recrystallized three times from alcohol (thereby of course losing its added molecule of hydrochloric acid) and then melted at 119°, and showed the other properties of 2,4,6-tribromoaniline.

Calculated for $C_5H_4NBr_3$: Br, 72.71; found, 73.11.

The action of bromine was tried on 3,5-dibromo-4-aminobenzophenone in certain preliminary studies which will be continued. No splitting apart of the two benzene nuclei takes place as with the corresponding hydrol, but perbromide bodies are formed.

This research will be continued in this laboratory and extended to other benzhydrol derivatives.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 69.]

THE ELECTRON CONCEPTION OF VALENCE. II. THE ORGANIC ACIDS.

BY K. GEORGE FALK.

Received April 10, 1911.

1. Introduction. 2. Theoretical Considerations. 3. Saturated Monobasic Acids. 4. Saturated Dibasic Acids. 5. Unsaturated Acids. 6. Aromatic Acids. 7. Summary.

1. Introduction.—The hypothesis of Sir J. J. Thomson, according to which the linkages or bonds between the atoms in a molecule are formed by the transfer of corpuscles, was developed mainly in relation to organic compounds in a preceding article.[1] It will be applied in this paper to the ionization relations of organic acids. The ionization constants ($K \times 10^5$) of the acids as calculated from the Ostwald dilution law, $K = \frac{\gamma^2}{v(1-\gamma)}$, in which v = the volume in cubic centimeters containing one mol of the acid, and γ = the degree of ionization found from the conductance ratio, will be used. The factors upon which the accuracy and reliability of K depend for any one acid at a definit temperature for a series of concentrations have been discussed in detail by Scudder.[2] Only those acids will be considered for which a fairly reliable value of K has been obtained. This eliminates the highly ionized acids for which K varies with change in concentration. The data refer to 25° and the results of a number of different observers have been used.[3]

[1] Falk and Nelson, THIS JOURNAL, 32, 1637–54 (1910).

[2] *J. Physic. Chem.*, 7, 293 (1903).

[3] Ostwald, *Z. physik. Chem.*, 3, 170, 241, 369 (1889). Bethman, *Ibid.*, 5, 385 (1890). Berthelot, *Ann. chim. phys.*, [6], 23, 43 (1891). Crum Brown and Walker, *Ann.*, 261, 116 (1891). Walker, *J. Chem. Soc.*, 61, 696 (1892). Walden, *Z. physik. Chem.*, 8, 448 (1891); 10, 646 (1892). Stohmann and Kleber, *J. prakt. Chem.*, 45, 480

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2. *Theoretical Considerations.*—The principles upon which the directions of the valences are assumed to depend were explained in the first paper. It may suffice to state here that for a single bond the corpuscle for the carbon-hydrogen union is assumed to pass from the hydrogen to the carbon, the former becoming positively charged, the latter negatively, while for the carbon-chlorine union, the corpuscle passes from the carbon to the chlorine. For a double or triple bond there are more possibilities of union between two atoms, but in general, one of the cases involving certain definit valence directions will represent the most stable form of the compound in question. The arrangement of the elements in the periodic system serves in general to indicate the electrical relations of the elements to each other in the production of a bond.

In considering the structures of the organic acids, it is evident that the α-carbon atom (the one combined directly with the carboxyl group) influences the ionization constant of the acid to the greatest extent. A classification of the acids will be given here, which depends upon the direction of the valences by which this α-carbon atom is combined with the other atoms in the molecule. This divides the acids into four general classes, which may be formulated as follows:

I. $\rightrightarrows C.CO_2H$; II. $\rightleftarrows C.CO_2H$; III. $\leftleftarrows C.CO_2H$; IV. $\leftleftarrows C.CO_2H$.

The acids belonging to class I are those in which three electropositive groups are combined with the α-carbon atom; those belonging to class II, two electropositive and one electronegative; to class III, one electropositive and two electronegative. The ionization constants are found to increase in the order of the classes I, II, III, IV. The acids represented by formula IV, such as trichloroacetic acid, are too highly ionized to give satisfactory dissociation constants, and will not be considered in detail here.

This method of consideration differs from the ordinary one, which attributes the variations of the ionization constant directly to the nature of the neighboring atoms or groups, in assuming that the influences determining the magnitude of the ionization constant are the positions of the electric charges or corpuscles. These positions indeed are determined by the nature of the adjacent atoms or groups, so that the new hypothesis is to be regarded as a development of the older idea, which serves to give it greater definitness. The "direction of the bonds or valences" and the arrows representing this direction are merely a convenient conven-

(1892). Hantzsch and Miolati, *Z. physik. Chem.*, 10, 23 (1892). Franke, *Ibid.*, 16, 482 (1895). Euler, *Ibid.*, 21, 264 (1896). Szyszkowski, *Ibid.*, 22, 173 (1897). Smith, *Ibid.*, 25, 194 (1898). Bone and Sprankling, *J. Chem. Soc.*, 77, 673 (1900). Lichty, *Ann.*, 319, 380 (1901). Bone, Sudborough and Sprankling, *J. Chem. Soc.*, 85, 540 (1904). Drucker, *Z. physik. Chem.*, 52, 642 (1905).

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tional method of expressing the location of the negative charge, which is always to be considered as located at the point of the arrow.

The influences exerted by the double or triple bond, according to the new point of view, are made up additively of the influences exerted by the two or three single bonds or valences. Thus, the ionization constant for maleic acid, having the formula[1] $HO_2C.CH \rightleftarrows CH.CO_2H$, depends mainly upon the identical directions of the valences making up the double bond, and that of fumaric acid, whose formula[1] is $HO_2C.CH \rightleftarrows CH.CO_2H$, differs from that of maleic acid since the directions of the valences of the double bond of the α-carbon atom lie in opposit directions.

The groups combined with the β-carbon atom, or the directions of the valences of this atom, doubtless influence the ionization constant; but as will be seen, this influence is in most case of small importance when compared with the influence exerted by the bonds of the α-carbon atom, and while the acids substituted in the β-position may have ionization constants lying between those for class I and class II, for example, there should be no doubt in most cases as to the class to which the acid should be assigned. The groups combined in the γ, δ, etc., positions doubtless exert an influence on the constants also, but this influence is negligible in the consideration of this classification.

Although the classification just given depends primarily upon the directions of the valences, the specific effect of certain groupings may be great enough at times to exert a predominating influence and obscure the relations just described. These effects, which are unquestionably present with every atom or group in an acid, are too small to be perceived with the present methods of experiment and calculation and therefore do not interfere when the acids are divided into the general classes depending on the directions of the valences of the α-carbon atom except, possibly, in individual cases.

Acids which contain an amino group will not be included in the discussion, and all acids containing sulfur have been omitted as well.

3. *Saturated Monobasic Acids.*—In the aliphatic acids containing only carbon and hydrogen in combination with the carboxyl group, the arrangement of the bonds of the α-carbon atom (that combined directly with the carboxyl group) may, as stated, be represented by the formula $\rightrightarrows C—CO_2H$, in which the direction of the heads of the arrows representing the bonds indicate the direction of the transfer of the negative corpuscles. The values of the constant ($K \times 10^5$) for these acids vary between 0.0011 and 0.0020 and include the following, arranged in the order of increasing values for the constant: pelargonic, caprylic, caproic, isobutyric, heptylic, isocaproic, butyric, valeric, ethylmethylacetic, iso-

[1] *Loc. cit.*, p. 1643.

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valeric, acetic, tetramethylenecarboxylic, and diethylacetic. The following acids and their dissociation constants contain the same bonds for the α-carbon atom as the acids just considered, but are substituted by halogens, hydroxyl groups, phenyl groups, etc., in the β-, γ-, or δ-positions: δ-chlorovaleric, 0.0020; benzoylpropionic, 0.0022; hydrocinnamic, 0.0023; levulinic, 0.0026; β-hydroxypropionic, 0.0031; β-chloropropionic, 0.0086; β-chlorobutyric, 0.0089; β-iodobutyric, 0.0090; β-bromopropionic, 0.0098; and eleven substituted β-hydroxypropionic acids,[1] 0.0015 to 0.0045. To these may be added phenylacetic, 0.0056, and hydroatropic, 0.0043, indicating that the phenyl group as a substituent exerts an influence on the ionization constants of acids similar to that exerted by the methyl, etc., groups.[2] The ionization constants for these acids are less than 0.005 except for the three β-halogen propionic and phenylacetic acids, and for these they are less than 0.01. The constitutive effect is evident here, but it is not great enough to mask the additive influence of the bonds (as will be seen presently with the α-halogen substituted acids). For the acids containing the grouping $\rightrightarrows$ C—CO_2H, the constant may be taken in general to lie between 0.001 and 0.005 with variations due to the constitutive effect of the substituting groups up to 0.01 and perhaps higher.[3]

The formula for the aliphatic acids containing a halogen or similar (negative) substituent in the α-position may be represented by $\rightleftarrows$ C—CO_2H. The acids belonging to this class which have been studied are iodoacetic, 0.075; α-bromobutyric, 0.106; α-bromopropionic, 0.108; bromoacetic, 0.138; α-chlorobutyric, 0.139; α-chloropropionic, 0.147; chloroacetic, 0.155; sulfocyanoacetic, 0.265; cyanoacetic, 0.370; and α,β-dibromopropionic, 0.67.[4] For acids of this class, the constant may be taken as lying between 0.1 and 0.4 unless modified very markedly by some constitutive influence.

Few acids containing two negative substituents in the α-position of the formula $\rightleftarrows$ C—CO_2H have been studied. α,α-Dibromopropionic, 3.3, and dichloroacetic, 5.2, are the only ones for which data were found. Acids containing three negative constituents in the α-position are too highly ionized for the purpose in view and do not give a satisfactory constant.

The constants for the acids so far considered may be summarized as follows: For the grouping $\rightrightarrows$ C—CO_2H, less than 0.01; for $\rightleftarrows$ C—

[1] Szyszkowski, *Loc. cit.*

[2] This coincides with the view advocated by Michael and Leighton as to the comparative influence of the phenyl and methyl groups. *Ber.*, **39**, 2792 (1906).

[3] Whether a β,β-dihalogen propionic acid would have a larger constant is a question which can be answered only by experiment.

[4] For the dilutions between 32 and 128 liters.

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CO_2H, 0.1–0.4; for $\rightleftarrows$ C—CO_2H, greater than 2. Individual substituents modify these values to a greater or less extent, but the differences between the three classes appear to be great enough to enable a decision to be reached as to the structure of a given acid in most cases.

A group of acids for which the constants lie between those for the acids containing the groupings $\rightrightarrows$ C—CO_2H and $\rightleftarrows$ C—CO_2H is known. This group comprizes the acids diisopropylglycolic, 0.013; lactic, 0.014; glycolic, 0.015; glyceric, 0.023; ethoxyacetic, 0.023; methoxyacetic, 0.034; mandelic, 0.042; phenoxyacetic, 0.076; and benzilic, 0.092. The OR (R = H or hydrocarbon radical) group is evidently the reason why these acids occupy an intermediate position between the acids containing no negative α-group and those containing one. This OR group is generally taken to have an effect similar to a negative group, and would therefore be formulated $\longrightarrow$OR in the acids Some of the acids approach the values for acids of the class $\rightleftarrows$ C—CO_2H, but for most of them the difference is so large that it must be assumed that either the OR group exerts a constitutive influence masking to a great extent the effect of the bonds or that there is some action[1] between the ether or hydroxyl oxygen and the hydrogen or other part of the carboxyl group which decreases the values of K for this group of acids as compared with the acids containing a different negative substituent in the α-position, resulting in a constant of from 0.01 to 0.1. It may be pointed out, however, that the class to which any given acid belongs may readily be ascertained as the composition taken in connection with the dissociation constant shows the structure of the α-carbon atom. An acid such as trichlorolactic, 0.465, must be formulated somewhat differently and probably is best represented by the structure $\begin{matrix} CCl_3 \nwarrow \\ HO \longleftarrow C—CO_2H \\ H \nearrow \end{matrix}$, or intermediate between the $\rightleftarrows$ C—CO_2H and $\rightleftarrows$ C—CO_2H classes, just as lactic acid is intermediate between the $\rightrightarrows$ C—CO_2H and $\rightleftarrows$ C—CO_2H classes.

4. Saturated Dibasic Acids.—Ostwald was the first to point out that the constants obtained by his dilution law for the organic dibasic acids referred to the first hydrogen ion which was formed from the acid and that the second hydrogen ionizes only in very di ute solutions, so that it does not enter into the constant as ordinarily determined. For some acids the second hydrogen begins to ionize appreciably at a dilution of about 500 liters, but the constant as determined experimentally in the usual way is found to increase rapidly with the dilution when this oc-

[1] Such as inner salt formation (oxonium), similar to that taking place with the amino acids.

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curs. A study of the constants for the dibasic acids may therefore follow the lines laid down for the monobasic acids by considering the carboxyl group containing the un-ionized hydrogen as a negative substituent.

Malonic acid, from this point of view, is carboxyl acetic acid and should belong to the $\rightleftarrows$ C—CO_2H class. Its constant is found to be 0.164.[1] The following substituted malonic acids, with their ionization constants, have been measured: dimethylmalonic, 0.076; α,α-tetramethylenedicarboxylic, 0.080; isobutylmalonic, 0.090; octylmalonic, 0.095; heptylmalonic, 0.102; butylmalonic, 0.103; propylmalonic, 0.112; hexamethylene tetracarboxylic (1, 1, 3, 3), 0.12; isopropylmalonic, 0.127; ethylmalonic, 0.127; benzylmalonic, 0.151; allylmalonic, 0.154; ethylmethylmalonic, 0.164; β-benzoylisosuccinic, 0.250; methylbenzylmalonic, 0.266. These acids evidently all belong to the class $\rightleftarrows$ C—CO_2H. Several acids, similarly constituted, have been found to give considerably greater dissociation constants. The value 0.74 was obtained for diethylmalonic and 1.46 for benzylethylmalonic. A comparison with the values obtained for ethylmethylmalonic (0.164) and for methylbenzylmalonic (0.266) indicates that the high values for the first two are due to some error as so large a difference is hardly to be expected for a change of CH_2 in these acids. On the other hand, the high values obtained for diallylmalonic acid (0.76) and dibenzylmalonic acid (4.1) may well be due to the constitutive effects of the substituting groups although measurements were not carried beyond a dilution of 256 liters.

Two substituted malonic acids have been measured which doubtless belong to the $\rightleftarrows$ C—CO_2H class: chloromalonic, 4, and α,α-trimethylenedicarboxylic, 2.1.

Succinic acid may be represented by the formula

$$(\alpha)HO_2C—CH_2 \longrightarrow CH_2—CO\ H(\beta).$$

If the α-hydrogen is ionized more easily than the β, succinic acid should belong to the $\rightleftarrows$ C—CO_2H class; if the the β more easily than the α, to the $\rightrightarrows$ C—CO_2H class. A study of the constants for succinic acid and the acids derived from it in which a hydrogen atom of one of the methylene groups is replaced by hydrocarbon radicals shows that the acids belong to the $\rightrightarrows$ C—CO_2H class (analogous to acetic acid), the negative carboxyl substituent in the β-position exerting a constitutive effect similar to that exerted by the halogens in the β-substituted propionic acids. The results for these acids are as follows: Succinic, 0.0068; isopropylsuccinic, 0.0075; asym. dimethylsuccinic, 0.0081; methylsuccinic, 0.0085; ethylsuccinic, 0.0086; isobutylsuccinic, 0.0088; propyl-

[1] Mean of the results given by Ostwald (0.158), Walden (0.163), and Bethmann (0.171). Berthelot found 0.165 at 17°.

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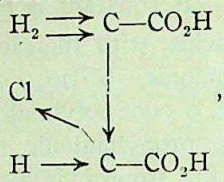
succinic, 0.0089; benzylsuccinic, 0.0091; and allylsuccinic, 0.0109. The three acids, bromosuccinic 0.278, chlorosuccinic 0.284, and sym. bromomethylsuccinic 0.478, evidently belong to the $\rightleftarrows$ C—CO_2 class analogous to chloroacetic acid and must be formluated (for the first named as example),  , in which each of the carbon atoms combined with a carboxyl has gained two and lost one corpuscle.

The symmetrical disubstituted succinic acids will not be taken up, as there are a number of isomers (stereochemical) known which are not sufficiently well characterized to make a discussion of them profitable. Furthermore, the fact that the three tartaric acids (*d*-, *l*-, and *i*-) have the same ionization constant (0.097) while mesotartaric acid has a different constant (0.060) shows that the presence of two asymmetric carbon atoms in an acid may result in differences in the values of the dissociation constants of acids which differ only in one being a racemic form (or mixture) and the other an internally compensated form, due doubtless to some effect at present entirely unknown. In the following tri- and tetra-substituted succinic acids, the presence of so many groups raises the constants to values greater than those found before for this class ($\rightrightarrows$ C—CO_2H) but still considerably less than for the class $\rightleftarrows$C—CO_2H: Trimethylsuccinic, 0.032; tetramethylsuccinic, 0.033; benzyldimethylsuccinic, 0.046; propyldimethylsuccinic, 0.055; ethyldimethylsuccinic, 0.056.

The higher homologs of the saturated dibasic acids may be considered as derived from the higher fatty acids containing a negative substituent which exerts only a minor influence upon the ionization constants as compared with the effect of the bonds. They should therefore belong to the $\rightrightarrows$ C—CO_2H class, and, in fact, the constants for those measured are found to lie between 0.0022 and 0.0059. The following acids are included and are arranged in the order of increasing values for K: Camphoric, sebasic, azelaic, suberic, ω,ω′-dipropylpimelic, ω,ω′-diisopropylpimelic, *n*-pimelic, ω,ω′-dimethylpimelic, ω,ω′-diethylpimelic, adipic, glutaric, ω,ω′-dibenzylpimelic, α-methylglutaric, α,α′-d ethylglutaric, β,β-dimethylglutaric, α,α′-dimethylglutaric, and β-methylglutaric.[1]

The effect of the hydroxyl group on the ionization constants of the dibasic acids is the same as for the monobasic acids, that is to say, the

[1] α,α-Dimethyl-β-hydroxyglutaric, 0.0108, may also be placed in this class, the substituting groups exerting a greater effect on the constant.

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negative character of the group raises the values, but for some constitutive or other effect the values are not less than where the negative substituent is a halogen atom or some other negative group. The constants for these hydroxy dibasic acids in which the second carboxyl group is not α to the first lie between those for the $\rightrightarrows$ C—CO_2H and the $\rightleftarrows$ C—CO_2H class, just as for the monobasic acids. This is illustrated by the acids: Malic, 0.039; mesotartaric, 0.060; and tartaric, 0.097. For those hydroxydibasic acids in which the two carboxyl groups are combined with the same carbon atom, the values of $K \times 10^5$ are found to correspond with those of the $\rightleftarrows$ C—CO_2H class; tartronic, 0.107, and benzyltartronic, 0.55, indicating that the effect of the hydroxyl group is not noticeable in the constants for these acids.

Some space may be devoted to the ester acids. With the higher homologs, the ethyl ester acids of sebasic 0.00143, suberic 0.00146, and adipic 0.0025, the constants show that they belong to the $\rightrightarrows$ C—CO_2H class, with the carboxyethyl group producing no appreciable effect. The ethyl ester acids of the malonic series, diethylmalonic 0.0231, dimethylmalonic 0.0304, methylmalonic 0.0387, ethylmalonic 0.0401, and malonic 0.0451, show that the action of the carboxyethyl group is similar to that of the hydroxyl (or ethoxyl, etc.) group in raising the constants above those for the $\rightrightarrows$ C—CO_2H class, but markedly below those for the $\rightleftarrows$ C—CO_2H class. If a specific constitutive reason is looked for, it may be due here, as indicated before, to the ether oxygen which is present in both groups.

The treatment of the succinic ester acids is complicated by the possibility of the existence of two isomeric ester acids in each case depending upon which of the two carboxyl group is esterified. The only substances of this series for which experimental values have been found are succinic ethyl ester acid 0.0030, and the methyl ester acids of succinic 0.0032, methylsuccinic 0.0039, *cis*-sym.-dimethylsuccinic 0.0046 (m. 38°), and *trans*-sym.-dimethylsuccinic 0.0061 (m. 49°). These results indicate that the ionization of these ester acids takes place from the group $\rightrightarrows$ C—CO_2H, the carboxyethyl group in the β-position exerting only a small constitutive influence.

Few measurements are at hand for the polybasic saturated acids. Tricarballylic acid, 0.022, and $\omega,\alpha,\beta,\omega'$-butanetetracarboxylic acid, 0.040, indicate that in all probability the ionization takes place as in the simplest fatty acids from the group $\rightrightarrows$ C—CO_2H and that the presence of the carboxyl groups raises the constants above those obtained for the unsubstituted acids but that they are still below those for

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the $\rightleftarrows$ C—CO_2H class. No light is thrown on the question as to which of the carboxyl groups furnishes the hydrogen ion.

5. *Unsaturated Acids.*—The unsaturated acids will be taken up in the same way as the saturated, and the double bond will be assumed to have the same effect upon the dissociation constant as if it were made up of two single bonds. It will be seen that a perfectly rational classification follows from this method of treatment and that the acids containing a double bond between two carbon atoms fall into the same groups depending upon the direction of the valences and considering their influence as purely additive, as the saturated acids. Caution must be used, however, with regard to the data for some of the isomeric acids, as the methods of isolating the pure substances had not been worked out very satisfactorily when some of the measurements were made.

The following monobasic acids containing a double bond between the α- and β-carbon atoms in four cases and between the β- and γ- in one case may first be quoted: Methylethylacrylic, 0.0011; sorbic,[1] 0.0017; hydrosorbic, 0.0024; trimethylacrylic, 0.0039; and acrylic, 0.0056. These acids evidently may be considered as belonging to the $\rightrightarrows$ C—CO_2H class, whether the α-carbon atom is combined with the other atoms in the molecule by means of three single bonds or one double bond and one single bond.

Before going on to the isomeric unsaturated acids, a number of dibasic acids may be considered as being closely related to the unsaturated monobasic acids. Without going into the details of the structures of these acids, the following general remarks may suffice. The acids to be considered may be assigned to the $\rightrightarrows$ C—CO_2H class, the second carboxyl group acting merely as a negative constituent (not in the α-position). The double bond in the α,β-position exerts an influence on the β-carbon atom and therefore on the ionization constant similar to that exerted in β-bromopropionic acid, for example. The constitutive effects of the different groups may be considerable in special cases. Methylitaconic, 0.0095; itaconic, 0.012; tetraconic, 0.014; methylethylitaconic, 0.015; methylphenylitaconic, 0.024; $\Delta(\beta,\gamma)$-hydromuconic, 0.010; dimethylglutaconic, 0.013; benzylglutaconic, 0.015; and glutaconic, 0.018. In these acids the factors mentioned above raise the ionization constants above the values found for the monobasic acids for the class indicated (just as in the saturated acids the same factors produce the same effect) but in no case is there a close approach to the constants for the class $\rightleftarrows$ C—CO_2H.

In the case of the isomeric unsaturated acids, a more detailed treatment is necessary. This can best be done with maleic and fumaric acids

[1] Contains two double bonds, one α,β, the other γ,δ.

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as here the substances were isolated in a state of purity early and therefore the measurements for finding the values of K may be considered to be accurate. Furthermore, the composition of the two acids is simple and it should be possible to draw perfectly definit conclusions. In the first paper[1] the conclusion was made very probable that fumaric acid should be assigned the structure $CO_2H.CH \rightleftarrows CH.CO_2H$ and maleic acid $CO_2H.CH \rightrightarrows CH.CO_2H$. Since the ionization constants refer only to one hydrogen ion and the carboxyl group may be treated as a negative substituent, fumaric acid should belong to the $\rightleftarrows C—CO_2H$ class, and as a matter of fact, its constant was found to be 0.093.[2] Maleic acid may, however, ionize in one of two ways: either from the $\rightleftarrows C.CO_2H$ group or from the $\rightrightarrows C.CO_2H$ group. The ionization constants for the acids belonging to these classes differ widely, and the value found for maleic acid, 1.17,[3] shows that the ionization takes place in the first of the methods indicated and that maleic acid may be classed with dichloroacetic acid, and fumaric acid with monochloroacetic acid in considering the ionization of the first hydrogen.

The data for the other isomeric unsaturated acids are in less satisfactory shape. For crotonic and isocrotonic acids, the work on the latter was done with an impure acid, containing some of the former. The constant for crotonic acid was found to be 0.0020, showing its structure to be best represented by the formula $CH_3CH \rightrightarrows CH.CO_2H$. This is the more stable form of the two acids and the difference in structure as regards the double bond in comparison with the double bond in fumaric acid, the stable form of the isomeric dicarboxylic ethylenes, must be due to the difference in the groups attached to the carbons joined by the double bond in the former case, and their identity in the latter. The results obtained for the chlorocrotonic acids, assuming the constants to be correct, are difficult to interpret and it appears that in this case the constitutive effects predominate over the additive effects of the bonds; especially as the conditions for the stable form of the double bond are not well known and must be considered separately for every case in which the number and arrangement of the atoms in the two halves of the molecule separated by the double bond are not symmetrical.

Mesaconic acid (methylfumaric acid) has the constant 0.079, or one similar to that for fumaric acid. The constant for citraconic acid (methylmaleic acid) was found to be 0.34, larger than that for mesaconic acid, but apparently not enough larger to belong to the $\rightleftarrows C—CO_2H$ class with certainty. The constant for ethylmaleic acid, 0.238, is of the same

[1] *Loc. cit.*, p. 1643.
[2] By Ostwald; Berthelot found 0.100 at 22°.
[3] By Ostwald; Berthelot found 1.10 at 22°.

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magnitude, and these two cases indicate that the substitution of an alkyl group for hydrogen in maleic acid decreases the constant considerably. The following results for substituted fumaric acids indicate clearly that these belong to the $\rightleftarrows C—CO_2H$ class: Ethylmesaconic, 0.093; isopropylmesaconic, 0.093; methylmesaconic, 0.094.

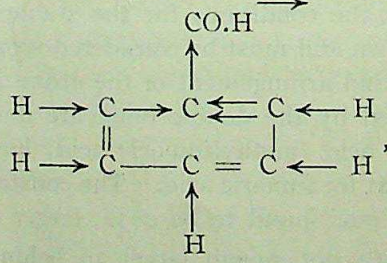
Benzalmalonic acid, 0.408, may be represented by the formula

$$C_6H_5CH \rightleftarrows C(CO_2H)—CO_2H.$$

The acids containing a triple bond can be disposed of briefly, as few have been measured. Tetrolic acid, 0.246, is to be best represented by the formula $CH_3.C \rightleftarrows C.CO_2H$, and phenylpropiolic acid, 0.59, by the similar formula $C_6H_5.C \rightleftarrows C.CO_2H$. The evidence obtained from the ionization constants leads to the same conclusion as to the usual structure of the triple bond, as did the study of the addition reactions with acetylenedicarboxylic acid considered in the first paper.[1]

6. *Aromatic Acids.*—The aromatic acids are taken to include those in which a carboxyl group from which the hydrogen is ionized is in direct combination with a carbon atom of the benzene nucleus. This carbon atom corresponds to the α-carbon atom in the saturated acids, and the bonds of this carbon atom are the ones which determin the ionization constant of the acid in question. It may be expected that a greater constitutive effect is exerted by the benzene ring on the constants. This is true to a certain extent as the general arrangement (or directions) of the valences and their influence upon each other between the carbon atoms in the ring are not known but the aromatic acids may be grouped in the same way as the aliphatic acids and the probable reciprocal influences of the bonds discussed without specifying the particular directions of all the valences. The benzene ring is assumed to contain alternate single and double bonds.

The ionization constant for benzoic acid was found to be 0.0067.[2] This indicates that benzoic acid belongs to the $\rightrightarrows C.CO_2H$ class, and that its graphic formula is



, the direction of the bonds indicated by dashes being unknown. Other aromatic acids in which the direction of the valences for carbon (1) is the same as for ben-

[1] *Loc. cit.*, p. 1644.

[2] By Euler, Ostwald found 0.0060.

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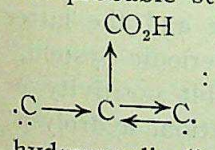
zoic acid, but for which the arrangement of the other bonds is unknown except that no strong constitutive effect is manifested by the two carbon atoms in position (2) and that therefore the direction of the bonds in these is not such as would be expected if only negative groups were combined with them, are the following: *p*-Hydroxybenzoic, 0.0029; vanillic, 0.0030; isovanillic, 0.0032; anisic, 0.0032; veratric, 0.0036; mesitylenic, 0.0048; *m*-toluic, 0.0051; *p*-toluic, 0.0052; methylsalicylic, 0.0082; *m*-hydroxybenzoic, 0.0083; 1,3,5-dihydroxybenzoic, 0.0091; and *p*-chlorobenzoic, 0.0093.

The following acids may be assigned to the same class as benzoic acid: *m*-Fluorobenzoic, 0.0136; *m*-bromobenzoic, 0.0137; *m*-chlorobenzoic, 0.0155; *m*-iodobenzoic, 0.0163; *m*-cyanobenzoic, 0.0199; isophthalic, 0.0287; *m*-nitrobenzoic, 0.0345; *o*-toluic, 0.0120; *p*-nitrobenzoic, 0.0396; and 1,2,4-resorcylic, 0.0515. In the first seven of these acids, the negative substituent in position (3) (or corresponding to the γ-position in the aliphatic acids) apparently exerts a constitutive effect on the constant comparable with some of the effects exerted by negative constituents in the β-position of the aliphatic acids. This effect may be due to the influence of the negative constituents on the direction of the valences between the carbon atoms (2) and (3), causing the valences for (2) to assume directions, which, if present in aliphatic acids, would cause similar changes in the constants. Similar reasoning may be applied to the last three acids.

The following acids must be assigned to the $\rightleftarrows$ C.CO_2H class, and the probable structure of part of the molecule may be formulated as



: Salicylic, 0.102; 1,2,5-hydroxysalicylic, 0.108; 1,2,3-hydroxysalicylic, 0.114; *o*-phthalic, 0.121; *o*-chlorobenzoic, 0.132; *o*-bromobenzoic, 0.145; *m,m*-dinitrobenzoic, 0.162; and *o*-nitrobenzoic, 0.616.

The only acid which appears to belong to the $\rightleftarrows$C.CO_2H class is 1,2,6-resorcylic, 5.0.

7. *Summary.*—Organic acids are divided into three classes in which the ionization constants ($K \times 10^5$) depend primarily upon the additive effects of the directive valences of the α-carbon atom: I. $\rightrightarrows$ C.CO_2H, ionization constants less than 0.01; II. $\rightleftarrows$ C.CO_2H, ionization constants 0.1–0.4; III. $\rightleftarrows$ C.CO_2H, ionization constants greater than 2.

Substituents may exert constitutive effects resulting in constants for the acids between the values given for the classes, but a study of the

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composition should indicate in most cases the class to which the acid may be assigned.

The effects of double and triple bonds are assumed to be due to the additive actions of the valence directions making up these bonds. Fumaric acid is thus shown to be comparable in strength to an acid such as monochloroacetic and maleic acid to dichloroacetic.

BOSTON, April, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

POLARITY OF ELEMENTS AND RADICALS MEASURED IN TERMS OF A LOGARITHMIC FUNCTION OF THE IONIZATION CONSTANT.

BY C. G. DERICK.

Received April 21, 1911.

Introduction.

In recent years polarity of elements and radicals has been employed to explain many chemical behaviors. Since the overthrow of the dualistic theory, polarity has remained a rather indefinit term, one of "chemical instinct" rather than mathematical exactness. In 1901 W. A. Noyes and A. C. Lyon[1] made the following statement: "If we suppose, what seems not to be improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of molecules, it would follow that elementary molecules as well may ionize into positive and negative parts." Ostwald[2] noted that certain groups and elements when substituted into acetic acid cause an increase or a decrease in its affinity constant. The former he called negative and the latter positive. Abegg,[3] in his article on "Valence and the Periodic System," stated that all elements are amphoteric, that is, exhibit positivity or negativity. He offers four criterions of polarity, ionization, hydrolysis, position in the periodic system, and finally the formula of the compound, in which case the maximum valence is the guide. This work supports the views of W. A. Noyes, referred to above. Finally, B. Flürscheim[4] has employed polarity in his studies of the distribution of affinity in the molecule of organic compounds. In a distinctly qualitative manner he has shown the value of the conception of polarity in interpreting certain properties of the organic molecule and it is in this branch of chemistry that polarity may be used most successfully in correlating chemical properties. In all these suggestions a more or less qualitative measure

[1] THIS JOURNAL, 23, 460 (1901).

[2] *J. prakt. Chem.*, 31, 433 (1885); *Z. physik. Chem.*, 3, 170, 418 (1889). Also Nernst, "Theoretische Chemie," 6th Auflage, p. 510.

[3] *Z. anorg. Chem.*, 39, 330 (1904).

[4] *J. Chem. Soc.*, 95, 718 (1909); 97, 84 (1910).

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of polarity has been implied. It is the purpose of this paper to discuss an exact definition for the terms positivity and negativity.

Definition of Positivity and Negativity.

In a general way, all elements and radicals will exhibit positivity if they cause hydroxyl ionization and negativity if they cause hydrogen ionization. But since some compounds do not appear to ionize appreciably this definition would have decided limitations. To overcome this difficulty, Ostwald suggested the use of an ionizing standard into which he substituted the element or radical. As referred to above, he chose acetic acid, but acetic acid is open to the objection that the negativity of negative groups is greatly magnified by the very negative carbonyl group—while the positivity of positive radicals is greatly decreased by the negativity of the carbonyl group. Hence a true relative quantitative comparison of the positivity and negativity of different radicals is impossible, using the standard, acetic acid. These facts may be easily seen if it is remembered that in using acetic acid as a standard we are in reality measuring the effect of different radicals upon the power of the carboxylic hydroxyl group to ionize hydrogen ions in the neighborhood of the strongly negative carbonyl group, as will be seen from the structural formula of substituted acetic acids, $R—CH_2—C\begin{matrix}\diagup O \\ \diagdown O—H\end{matrix}$. Such a standard is also open to the objection that all elements and radicals cannot be easily substituted into it, but this objection will hold for nearly every standard that may be chosen.

With these points in mind, the author has chosen water as the most satisfactory standard into which different elements and radicals may be substituted in order to determine their polaric nature. In water we have the hydrogen and hydroxyl ionizations balanced, that is, water is an amphoteric electrolyte which possesses equal negativity and positivity. Further, when a hydrogen of water has been replaced by a radical we are free to determine its true negativity or positivity without the influence of other groups. Using this standard, we may obtain a quantitative comparison of the negativity or positivity of different radicals as well as of the same radical, since most radicals appear to be amphoteric.[1] Hence we may give the following definitions:

1. An element or radical possesses positivity if, when it is substituted for a hydrogen of water, it increases the hydroxyl ionization. It is therefore said to be positive.

2. An element or radical possesses negativity if, when it is substituted for a hydrogen of water, it increases the hydrogen ionization. It is therefore said to be negative.

[1] See above references to W. A. Noyes and Abegg. C. Worth, Doctor's Thesis, Karlsruhe (1910).

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In other words, a positive radical increases the affinity constant K*b* while a negative group increases the affinity constant K*a* for water. Since some elements and most radicals show a measurable positive and negative nature,[1] it will often be found that both K*a* and K*b* for water are increased by substitution of a radical for hydrogen.

Since the free energy change—rather than the total energy change—is the best measure of chemical affinity, the affinity constant K is chosen as the measure of positivity and negativity. For the decrease in free energy which accompanies any chemical reaction we have, according to the second law of thermodynamics, the expression $A = R\,T\,ln\,K$, in which

A is the free energy of ionization,
R is the gas constant,
T is the absolute temperature, and
K is the ionization constant (Ostwald's "affinity constant" = 100 K).

From this expression it is evident that the free energy of ionization is a logarithmic function of K, since R is a constant. Therefore positivity and negativity of groups must be measured in terms of the logarithmic function of K*b* or K*a*, respectively.

Since polarity is measured in terms of a logarithmic function of K, it is clear that it must vary with the temperature, since K varies with T. The expression by which K varies with the temperature is $d\,ln\,K = q\frac{dT}{RT^2}$, in which

K is the affinity constant,
q is the heat of ionization,
dT is the change of temperature, and
R is the gas constant.

If the integration is performed between given limits of temperature T_1 and T_2 with the assumption that q is constant over this range of temperature, the following expression is obtained:

$$ln K_2 - ln K_1 = \frac{q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

By means of this equation, after measuring K_1 and K_2 at the temperatures T_1 and T_2, respectively, the value of q may be calculated without direct measurements and hence K may be calculated at any desired temperature, as restricted above. However, if q is not constant over the desired range of temperatures, the manner in which q varies with T must be determined and substituted in the differential equation and the latter integrated, when a perfectly general equation for the given substance will be obtained. With such an equation we have the means of determining how polarity varies with the temperature.

Since the affinity constant is chosen at the measure of polarity, the

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values given in the following tables will hold for those cases only where the mass law holds. In other words, the values are true for the radicals causing weak ionization in water solution at not too great concentrations. In the case of other solvents or strong electrolytes the polarity of a given radical must be determined under the given conditions of temperature, pressure, solvent and concentration.

Finally, this quantitative measure of polarity may be considered as made up of two factors which van't Hoff calls the direct space action and the indirect action (*i. e.*, through intervening carbon atoms) of radicals. This will be developed more fully later. Such a measure of polarity is justified from the standpoint that it will serve to correlate many isolated facts of organic chemistry, as will be shown in the following papers.

Explanation of the Following Tables of Polarity.

In the theoretical discussion, we found that the free energy of ionization was equal to $R\,T\,ln\,K$. A review of the following tables will show that the logarithm in this expression is minus in sign in the case of practically every organic compound. This means that an organic acid (base) will not of itself pass from unit concentration of the unionized form to unit concentration of its ions, but to cause this change work must be done on the acid (base). This work is equal to $R\,T\,ln\,K$. Obviously the greater the ionization of such an acid, the smaller will be the value of $R\,T\,ln\,K$. But, the greater the negativity (positivity) of a group substituted into water the greater will be its ionization. In the case of the organic compounds, therefore, those groups having the greatest polarity will give the smallest values for the free energy of ionization when substituted into water. Because of this fact, it seems better to define the negativity (Θ) and the positivity (ϕ) as equal to $-\frac{1000}{\log K}$. Thus the polaric constants Θ and ϕ are inversely proportional to the free energy of ionization and the value of the free energy of ionization in calories may be determined by multiplying $1/\Theta$ and $1/\phi$ by $a\,RT\,(-1000)$, in which

a is the factor necessary to change the natural logarithm to the Brigg's logarithm (2.30258).

R is the gas constant (1.986 calories), and

T is the absolute temperature (273 + 25).

The use of such a quantitative measure of polarity and other reasons for choosing the free energy of ionization rather than the ionization constant as the measure of the same will be given in subsequent papers. Finally, no attempt has been made to determine the probable error in the constants Θ and ϕ, but that they are accurate enough for the purpose of generalization in the field of organic chemistry will be shown later.

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POLARITY OF ORGANIC RADICALS AT 25° IN WATER SOLUTION.

Name of radical.	Formula of radical.	K. Ka	Log K.	θ.	φ.
I. Hydrocarbon radicals:					
Chloral hydrate	CCl_3CHOH—	$(K_a^{18°} =)1.0 \times 10^{-11}$	—11.000	90.9	
Phenyl	C_6H_5—	1.3×10^{-10}	— 9.886	101.5	
o-Chlorophenyl	$C_6H_4(Cl)$—	7.7×10^{-10}	— 9.113	109.8	
p-Chlorophenyl	$C_6H_4(Cl)$—	4.1×10^{-10}	— 9.387	106.5	
p-Nitrophenyl	$(NO_2)C_6H_4$—	7.0×10^{-8}	— 7.155	139.7	
p-Cyanophenyl	$(CN)C_6H_4$—	1.3×10^{-8}	— 7.886	126.6	
II. Acyl radicals:					
Formyl (aldehyde radical)	HCO—	2.14×10^{-4}	— 3.670	272.4	
Acetyl (ketone radical)	CH_3CO—	1.86×10^{-5}	— 4.731	211.0	
Propionyl	C_2H_5CO—	1.45×10^{-5}	— 4.839	206.6	
n-Butyryl	C_3H_7CO—	1.56×10^{-5}	— 4.807	208.0	
Isobutyryl	$(CH_3)_2CHCO$—	1.60×10^{-5}	— 4.796	208.4	
n-Pentyl	C_4H_9CO—	1.60×10^{-5}	— 4.796	208.4	
Isopentyl	$(CH_3)_2CH : CH_2.CO$—	1.70×10^{-5}	— 4.770	209.6	
Trimethylacetyl	$(CH_3)_3C.CO$—	9.78×10^{-6}	— 5.010	199.6	
Capronyl	$CH_3(CH_2)_4CO$—	1.45×10^{-5}	— 4.839	206.3	
Oenanthyl	$CH_3(CH_2)_5CO$—	1.46×10^{-5}	— 4.836	206.7	
Capryl	$CH_3(CH_2)_6CO$—	1.44×10^{-5}	— 4.842	206.3	
Pelayonyl	$CH_3(CH_3)_7CO$—	1.12×10^{-5}	— 4.951	202.0	
III. Olefine unsaturated acyl radicals:					
Acrylyl	$CH_2=CH—CO$—	5.6×10^{-5}	— 4.252	235.0	
α-β-Pentenyl	$C_2H_5CH=CHCO$	1.48×10^{-5}	— 4.830	206.8	
β-γ-Pentenyl	$CH_3CH=CH.CH_2CO$—	3.35×10^{-5}	— 4.475	223.5	
γ-∂-Pentenyl	$CH_2=CH.(CH_2)_2CO$—	2.09×10^{-5}	— 4.680	213.2	

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IV. Halogen substituted acyl radicals:				
α-Chlorobutyryl	$C_2H_5CHCl—CO—$	1.39×10^{-3}	— 2.857	350.0
β-Chlorobutyryl	$CH_3CHClCH_2CO—$	8.59×10^{-5}	— 4.066	246.0
γ-Chlorobutyryl	$CH_2O(CH_2)_3CO—$	3.0×10^{-5}	— 4.523	220.8
δ-Chlorovaleryl	$CH_2O(CH_2)_3CO—$	2.04×10^{-5}	— 4.689	213.0
α-Bromoacetyl	$CH_2BrCO—$	1.38×10^{-3}	— 2.860	349.5
β-Bromopropionyl	$CH_2BrCH_2CO—$	9.8×10^{-5}	— 4.009	249.3
γ-Bromobutyryl	$CH_2Br(CH_2)_2CO—$	2.6×10^{-5}	— 4.585	217.8
δ-Bromobutyryl	$CH_2Br(CH_2)_3CO—$	1.91×10^{-5}	— 4.719	212.0
Iodoacetyl	$CH_2ICO—$	7.5×10^{-4}	— 3.125	320.0
β-Iodopropionyl	$CH_2BrCH_2CO—$	9.0×10^{-5}	— 4.046	247.0
γ-Iodobutyryl	$CH_2Br(CH_2)_2CO—$	2.3×10^{-5}	— 4.638	215.3
δ-Iodovaleryl	$CH_2Br(CH_2)_3CO—$	1.71×10^{-5}	— 4.767	209.8
V. Hydroxy acyl radicals:				
α-Hydroxypropionyl	$CH_3CHOH.CO—$	1.38×10^{-4}	— 3.860	259.0
β-Hydroxypropionyl	$CH_2OHCH_2CO—$	3.1×10^{-5}	— 4.509	222.0
γ-Hydroxybutyryl	$CH_2OH(CH_2)_2CO—$	1.93×10^{-5}		
VI. Alkoxy acyl radicals:				
Methoxyacetyl	$CH_3O.CH_2.CO—$	3.0×10^{-4}	— 3.523	283.9
Ethoxyacetyl	$C_2H_5O.CH_2.CO—$	2.34×10^{-4}	— 3.631	275.2
VII. Carboxyl substituted acyl radicals:				
Malonyl (carboxy acetyl)	$HO_2C.CH_2CO—$	1.64×10^{-3}	— 2.785	359.2
Succinyl (β-carboxypropionyl)	$HO_2C.(CH_2)_2CO—$	6.7×10^{-5}	— 4.174	239.3
Glutaryl (γ-carboxybutyryl)	$HO_2C(CH_2)_2CO—$	4.7×10^{-5}	— 4.328	231.0
Adipyl (δ-carboxyvaleryl)	$HO_2C(CH_2)_3CO—$	3.7×10^{-5}	— 4.432	225.3
Pimelyl (ε-carboxycapronyl)	$HO_2C(CH_2)_4CO—$	3.23×10^{-5}	— 4.491	222.7
Suberyl (ζ-carboxyenanthyl)	$HO_2C(CH_2)_5CO—$	2.99×10^{-5}	— 4.524	220.8
Azelayl (η-carboxycaprylyl)	$HO_2C(CH_2)_6CO—$	2.5×10^{-5}	— 4.602	217.2
Sebacyl (θ-carboxypelayonyl)	$HO_2C(CH_2)_7CO—$	2.38×10^{-5}	— 4.624	216.0

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POLARITY OF ORGANIC RADICALS AT 25° IN WATER SOLUTION (*Continued*).

Name of radical.	Formula of radical.		K.	Log K.	θ.	φ.
VIII. Carboxalkyl substituted acyl radicals:						
Carboxethyl acetyl.....	$C_2H_5O_2C.CH_2CO$—		4.51×10^{-4}	— 3.346	299.0	
Carboxethyl-β-propionyl.....	$C_2H_5O_2C.(CH_2)_2CO$—		3.02×10^{-5}	— 4.520	221.0	
Carboxmethyl-β-propionyl....	$CH_3O_2C(CH_2)_2CO$—		3.23×10^{-5}	— 4.491	222.7	
Carboxethyl-ζ-enanthyl.....	$C_2H_5O_2C(CH_2)_5CO$—		1.46×10^{-5}	— 4.836	206.7	
Carboxethyl-θ-pelargonyl.....	$C_2H_5O_2C(CH_2)_7CO$—		1.43×10^{-5}	— 4.845	206.4	
IX. Aminoacyl radicals:						
Aminoacetyl.....	NH_2CH_2CO—	$Kb =$	2.7×10^{-12}	—11.569		86.4
		$Ka =$	1.8×10^{-10}	— 9.745	102.6	
α-Aminopropionyl.....	$CH_3CH(NH_2)CO$—	$Ka =$	1.9×10^{-10}	— 9.721	102.7	
		$Kb =$	$5.1 = 10^{-12}$	—11.293		88.5
X. (N)-Alkylaminoacyl radicals:						
(N)-Methylaminoacetyl	$CH_3NH.CH_2CO$—	$Ka =$	1.2×10^{-10}	— 9.921	100.7	
		$Kb =$	1.7×10^{-12},	—11.770		85.0
(N)-Dimethylaminoacetyl....	$(CH_3)_2N.CH_2CO$—	$Ka =$	1.3×10^{-10}	— 9.886	101.2	
		$Kb =$	9.8×10^{-13}	—12.009		82.7
XI. (N)-Arylaminoacyl radicals:						
Anilino-α-propionyl.....	$CH_3CH(C_6H_5NH)CO$—		2.2×10^{-5}	— 4.658	214.8	
Anilino-β-propionyl.....	C_6H_5NH—$(CH_2)_2CO$—		4.0×10^{-6}	— 5.398	185.3	
o-Toluino-α-propionyl.....	$\overset{2}{CH_3}C_6H_4NH$—$CH(CH_3)CO$—		3.9×10^{-5}	— 4.409	227.0	
o-Toluino-β-isobutyryl.....	$\overset{2}{CH_3}C_6H_4NH.C(C_2H_3)_2CO$—		4.0×10^{-6}	— 5.398	185.3	
p-Toluino-α-propionyl.....	$\overset{4}{CH_3}C_6H_4NH.CH(CH_3)CO$		7.0×10^{-6}	— 5.155	197.7	
p-Toluino-β-propionyl.....	$\overset{4}{CH_3}C_6H_4NH.(CH_2)_2CO$—		2.0×10^{-6}	— 5.699	175.4	
XII. (N)-Acetarylaminoacyl radicals:						
Acetanilino-α-propionyl.....	$C_6H_5N(COCH_3)CH(CH_3)CO$—		1.25×10^{-4}	— 3.903	256.3	

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Acetanilino-β-isobutyryl.....	$C_6H_5N(COCH_3)C(CH_3)_2$—CO—	2.9×10^{-5}	— 4.538	220.0
Aceto-o-toluino-α-propionyl...	$CH_3^2C_6H_4N(COCH_3)CH(CH_3)CO$—	1.04×10^{-4}	— 3.983	251.0
Aceto-o-toluino-β-isobutyryl..	$CH_3^2C_6H_4N(COCH_3)C(CH_3)_2CO$—	2.1×10^{-5}	— 4.678	213.7
Aceto-p-toluino-α-isobutyryl..	$CH_3^4C_6H_4N(COCH_3)C(CH_3)_2CO$—	9.5×10^{-5}	— 4.022	248.4
Aceto-p-toluino-β-isobutyryl..	$CH_3^4C_6H_4N(COCH_3)CH_2.CH(CH_3)CO$—	2.3×10^{-5}	— 4.638	215.2
XIII. Aromatic acid radicals:				
Benzoyl.....	C_6H_5CO—	6.9×10^{-5}	— 4.161	240.0
Phenylacetyl	$C_6H_5CH_2CO$—	5.3×10^{-5}	— 4.276	233.8
Phenyl-β-propionyl.....	$C_6H_5(CH_2)_2CO$—	2.3×10^{-5}	— 4.638	215.2
o-Toluyl.....	$CH_3^2C_6H_4CO$—	1.25×10^{-4}	— 3.903	256.4
m-Toluyl.....	$CH_3^3C_6H_4CO$—	5.1×10^{-5}	— 4.293	232.7
p-Toluyl.....	$CH_3^4C_6H_4CO$—	5.1×10^{-5}	— 4.293	232.7
Mesityl.....	$(CH_3)_2^{3,5}C_6H_3CO$—	4.8×10^{-5}	— 4.319	226.5
α-Naphthyl.....	$C_6H_4.C_4H_3CO$—	2.0×10^{-3}	— 2.699	374.6
β-Naphthyl.....	$C_6H_4C_4H_3CO$—	6.0×10^{-5}	— 4.222	236.6
Cinnamyl.....	$C_6H_5CH=CHCO$—	3.5×10^{-5}	— 4.456	224.6
Phenylpropiolyl	$C_6H_5C=C$—CO—	5.9×10^{-3}	— 2.959	337.7
o-Chlorobenzoyl.....	ClC_6H_4CO—	1.32×10^{-3}	— 2.880	347.0
m-Chlorobenzoyl.....	ClC_6H_4CO—	1.35×10^{-3}	— 2.810	355.5
p-Chlorobenzoyl.....	ClC_6H_4CO—	9.3×10^{-5}	— 4.032	247.8
Salicyl.....	HOC_6H_4CO—	1.04×10^{-3}	— 2.983	325.0
m-Hydroxybenzoyl.....	HOC_6H_4CO—	8.33×10^{-5}	— 4.078	244.8
p-Hydroxybenzoyl.....	HOC_6H_4CO—	2.9×10^{-5}	— 4.538	220.2

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POLARITY OF ORGANIC RADICALS AT 25° IN WATER SOLUTION (*Continued*).

Name of radical.	Formula of radical.		K.	Log K.	θ.	φ.
Phthalyl	$^{2}HOOCC_6H_4CO—$		1.21×10^{-3}	— 2.917	342.4	
Isophthalyl	$^{3}HOOCC_6H_4CO—$		2.9×10^{-4}	— 3.538	282.6	
Terephthalyl	$^{4}HOOCC_6H_4CO—$		1.5×10^{-4}	— 3.824	261.5	
o-Nitrobenzoyl	$^{2}NO_2C_6H_4CO—$		6.3×10^{-3}	— 2.199	450.5	
m-Nitrobenzoyl	$^{3}NO_2C_6H_4CO—$		3.45×10^{-4}	— 3.462	290.0	
p-Nitrobenzoyl	$^{4}NO_2C_6H_4CO—$		4.0×10^{-4}	— 3.398	294.0	
o-Aminobenzoyl	$^{2}NH_2C_6H_4CO—$	$Ka =$	1.06×10^{-5}	— 4.975	201.0	
		$Kb =$	1.38×10^{-12}	—11.860		84.3
m-Aminobenzoyl	$^{3}NH_2C_6H_4CO—$	$Ka =$	1.63×10^{-5}	— 4.788	209.0	
		$Kb =$	1.22×10^{-11}	—10.914		9.61
p-Aminobenzoyl	$^{4}NH_2C_6H_4CO—$	$Ka =$	1.21×10^{-5}	— 4.917	203.3	
		$Kb =$	2.33×10^{-12}	—11.633		86.0
(N) Methyl-*o*-aminobenzoyl	$^{2}CH_3NHC_6H_4CO—$	$Ka =$	4.6×10^{-6}	— 5.337	187.0	
		$Kb =$	8.5×10^{-13}	—12.068		82.8
(N) Methyl-*o*-aminobenzoyl	$^{3}CH_3NHC_6H_4CO—$	$Ka =$	8.0×10^{-6}	— 5.096	196.0	
		$Kb =$	1.10×10^{-11}	—10.959		91.3
(N) Methyl-*p*-aminobenzoyl	$^{4}CH_3NHC_6H_4CO—$	$Ka =$	8.2×10^{-6}	— 5.036	198.4	
		$Kb =$	1.52×10^{-12}	11.818		84.5
XIV. Acyl radical of nitrogen:						
Nitroso	O = N—		4.5×10^{-4}	— 3.347	298.8	

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XV. Basic radicals of nitrogen:					
			Kb		
Ammonium	NH_4—	=	1.87×10^{-5}	— 4.728	211.4
Methylammonium	CH_3NH_2—		5.0×10^{-4}	— 3.301	302.8
Dimethylammonium	$(CH_3)_2NH_2$—		7.4×10^{-4}	— 3.131	319.0
Trimethylammonium	$(CH_3)_3NH$—		7.4×10^{-5}	— 4.131	242.0
Ethylammonium	$C_2H_5NH_2$—		5.6×10^{-4}	— 3.252	307.2
Propylammonium	$C_3H_7NH_2$—		4.7×10^{-4}	— 3.328	298.5
Isopropylammonium	$(CH_3)_2CHNH_2$—		5.3×10^{-4}	— 3.276	305.2
Isobutylammonium	$(CH_3)_2CH.CH_2NH_2$		3.1×10^{-4}	— 3.509	284.7
Isoamylammonium	$(CH_3)_2CH.(CH_2)_2NH_2$—		5.0×10^{-4}	— 3.301	302.8
Phenylammonium	$C_6H_5NH_2$—		4.6×10^{-10}	— 9.337	107.0
o-Toluylammonium	$CH_3.C_6H_4NH_2$—		3.3×10^{-10}	— 9.482	105.5
m-Toluylammonium	$CH_3C_6H_4NH_2$—		6.0×10^{-10}	— 9.222	108.3
p-Toluylammonium	$CH_3C_6H_4NH_2$—		2.0×10^{-9}	— 8.699	115.0
Phenylmethylammonium	$C_6H_5(CH_3)NH_2$—		7.4×10^{-9}	— 8.131	123.0
Urea	$NH_2CO.NH_2$—		1.5×10^{-14}	—13.824	72.2
Anilinoammonium	$C_6H_5NH.NH_2$—	Kb^{40} =	1.6×10^{-9}	— 8.796	125.0
Aminoammonium	$NH_2.NH_2$—		3.0×10^{-6}	— 5.523	180.8
Semicarbazine	$NH_2CO.NH.NH_2$—		2.7×10^{-11}	—10.569	94.6
Pyridine	CH=CH—CH=CH—CH=NH—		2.28×10^{-9}	— 8.642	115.6
XVI. Acyl sulfur radicals:					
			Ka		
Sulfurous	HOSO—		1.6×10^{-2}	— 1.796	557.0

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The constants Θ and ϕ given in these tables are for the solvent water at 25°. The data from which they were calculated were taken from "Affintatmessungen an schwachen Säuren and Basen," by H. Lunden.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

APPLICATION OF POLARITY MEASURED IN TERMS OF A LOGARITHMIC FUNCTION OF THE IONIZATION CONSTANT. I. THE USE OF POLARITY IN THE EXPLANATION OF THE REACTIONS OF ALDEHYDES AND KETONES.

BY C. G. DERICK.

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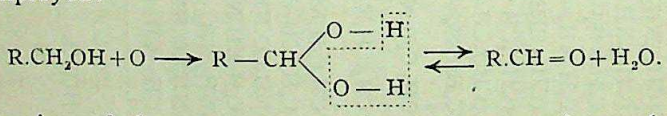
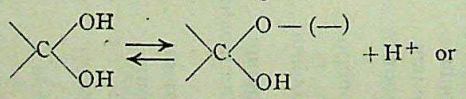
I. Mechanism of Dehydration of the Dihydroxy Form of Aldehydes and Ketones.

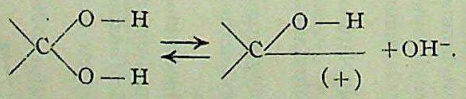
The quantitative measure of polarity developed in the previous paper may be applied to the reactions of aldehydes and ketones, so that useful generalizations may be drawn, as the following will illustrate. To apply this measure a neutral aldehyde or ketone is defined as a compound whose ionization constant lies in the order 10^{-14} at 25° for water solutions. The acid or basic aldehyde must therefore have Ka or Kb greater than 9.99×10^{-14}.

In the explanation of the formation of aldehydes and ketones from primary or secondary alcohols, respectively, the following mechanism is usually employed:

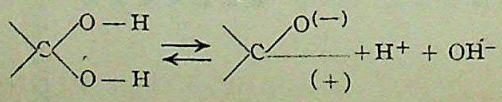


The mechanism of the spontaneous dehydration may be explained as follows for neutral aldehydes or ketones. These substances in the dihydroxy forms are amphoteric, ionizing thus:





But if the above ionization occurs upon the same carbon atom, we have:



If the hydrogen and hydroxyl ionization occur simultaneously in water

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solution, the concentration of at least one of the ions must be reduced to that of water under the given conditions due to the reaction

$$H^+ + OH^- \rightleftarrows H_2O.$$

There would be left in solution $>C<^{O-H}_{O-H}$ and the ion $>C<^{O\overset{(-)}{}}_{(+)}$, but since upon isolation we obtain the aldehyde or ketone in the form $>C=O$, we know that another equilibrium is present, namely,

$$>C<^{O\overset{(-)}{}}_{(+)} \rightleftarrows >C=O.$$

Therefore a water solution of an aldehyde contains at least the following molecular species:

$$>C<^{O-H}_{O-H},\ >C<^{O\overset{(-)}{}}_{(+)},\ >C=O,\ H^+,\ OH^- \text{ and } H_2O.$$

Obviously the active form of the aldehyde is $>C<^{O\overset{(-)}{}}_{(+)}$ and the mechanism of the dehydration of the dihydroxy forms of aldehyde and ketones is easily explained.

This explanation may be tested in the following manner: It was shown under the measure of polarity that negative groups increased the H^+ ionization and decreased the OH^- ionization of a given amphoteric electrolyte. The effect of substitution of negative groups into neutral aldehydes or ketones must be to increase the hydrogen and decrease the hydroxyl ionizations. If such substitution decreases the concentration of the hydroxyl ionization to that of water under the given conditions, the dihydroxy form should be completely stable and give the following equilibrium in solution:

$$>C<^{OH}_{OH} \rightleftarrows >C<^{O\overset{(-)}{}}_{OH} + H^+$$

If the negativity of the molecule is not sufficiently great to prevent the tendency of the OH^- ionization becoming greater than that of water, then the following equilibria must exist in solution:

$$>C<^{O-H}_{O-H} \rightleftarrows >C<^{O\overset{(-)}{}}_{O-H} + H^+,$$

$$>C<^{OH}_{OH} \rightleftarrows >C<^{O\overset{(-)}{}}_{(+)} + (H^+ + OH^-),\ H^+ + OH^- \rightleftarrows H_2O,$$

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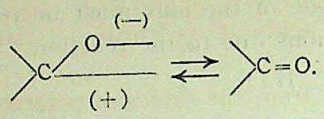
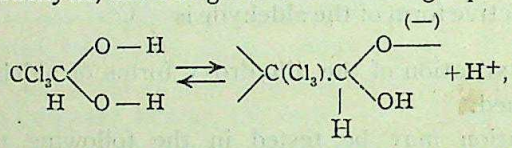


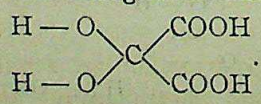
In such a case the aldehyde or ketone must exist mainly in the inactive form, $>C=O$, and its water solution will have $Ka > Kb$ or Ka for aldehydes $> Ka$ for water. This is apparently the case in formaldehyde and acetaldehyde, which give $Ka^{\circ} = 0.7$ and 1.4×10^{-14}, respectively, while that of water at zero degrees is 0.12×10^{-14}. This shows that the negativity of the molecule is predominant, so that the tendency to ionize H^+ is greater than that to give the hydroxyl ion, OH^-, yet the negativity is not sufficient to reduce the tendency to produce hydroxyl ions, OH^-, to that of water under the same conditions.

In the case of chloral hydrate, however, the negativity, $\Theta_{18^{\circ}} = 134$, for chlorine of the molecule is sufficient to reduce the tendency of the production of hydroxyl ions to that of water under the same conditions. Hence the aldehyde is stable in the dihydroxy form and is a much stronger acid than formaldehyde, since it gives the following equilibrium in water:



$Ka^{\circ} = 0.4 \times 10^{-11}$ and $Ka^{18^{\circ}} = 1 \times 10^{-11}$ for chloral hydrate, bearing out the above conclusions.

If we choose groups of greater negativity than chlorine and substitute them into neutral aldehydes or ketones, the dihydroxy form should be stable. In the paper on the measure of polarity Θ is defined as proportional to $1/\log K$. If we compare carbonic and hypoiodous acids we find for $\Theta_{18^{\circ}}$, HOOC : Cl $= 1/6.516 :: 1/7.422 = 1.138 : 1$. It is seen that the carboxyl group is more negative than chlorine, yet the accuracy of this ratio may be questioned.[1] Hence the substitution of the carboxyl group into neutral aldehydes and ketones should make the dihydroxy form stable at ordinary temperature. In the case of glyoxalic acid, $\left(\begin{matrix} H-O \\ H-O \end{matrix}\!\!>\!C\!-\!\underset{H}{}\!-COOH\right)$, we have the hydrogen of formaldehyde substituted by the strongly negative carboxyl group and the dihydroxy form of the aldehyde is stable, so stable toward dehydration that all attempts to dehydrate it have resulted in its complete decomposition. The same facts are true concerning mesoxalic acid,



[1] J. Walker, *Z. physik. Chem.*, 49, 82 (1904); 51, 708 (1905); 57, 600 (1906).

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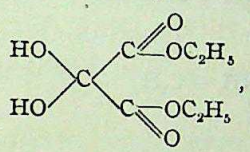
The ionization constants of these two acids at 25° are 5×10^{-4} and 5×10^{-3}, respectively.

From acetic and formic acids, we find from the tables of polarity that Θ for the acetyl and aldehyde radicals is 211 and 272.4, respectively. By comparing the normal paraffin acids it will be seen that hydrogen and methyl radicals have a small positive effect, so that the true negativity of the carbonyl radical would be greater than 272.4. Thus, if carbonyl groups are substituted into a neutral aldehyde or ketone, the dihydroxy form would be more stable since the carbonyl radical is much more negative than the chlorine radical (Θ_{18} for HC = O : Cl = 272.4 : 134.5). The dihydroxy form of diethyl mesoxalate,



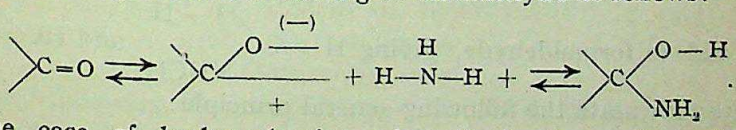
is stable below 58°.

These illustrations serve to show the connection between polarity and the form in which certain grouping of atoms may exist. They also serve as an indication of the conditions under which certain forms of compounds may be isolated.

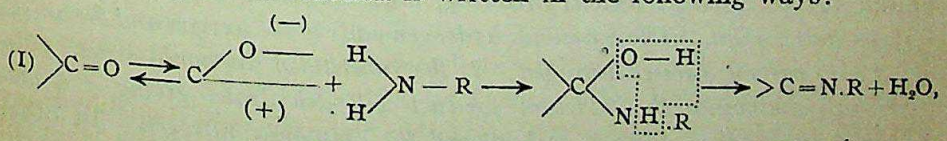
II. Oxime, Hydrazone and Semicarbazone Formations.

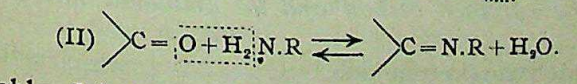
A quantitative measure of polarity furnishes us with a means of stating generalization in place of endless detail. This fact is well illustrated by the additive reactions of aldehydes and ketones.

Ammonia is represented as adding to an aldehyde as follows:



In the case of hydroxylamine, phenylhydrazine and semicarbazine and an aldehyde the reaction is written in the following ways:





Unquestionably, I is the correct reaction since we are dealing with substituted ammonias and it is the same NH_2 group which reacts in every case as in NH_3. That hydroxylamine, semicarbazine, phenylhydrazine, hydrazine, ethylamine and methylamine are substituted ammoniums possessing a similar NH_3 group is seen by the following scheme:

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	ϕ.
H_2NH-H	211.4
H_2NH-OH	<211.4
$H_2NH-NHCONH_2$	94.6
$H_2NH-NHC_6H_5$	125.0
H_2NH-NH_2	180.8
$H_2NH-C_2H_5$	307.2
H_2NH-CH_3	302.8

Taking ammonium as unity, the relative positivity is:
$NH_4 : NH_3.NH.CONH_2 : NH_3.NHC_6H_5 : NH_3.NH_2 : NH_3C_2H_5 : NH_3CH_3 =$
$1 : 0.447 : 0.592 : 0.855 : 1.452 : 1.433$.

It will be noted that those molecules whose positivity is less than that of ammonia will add to neutral aldehydes or ketones and dehydration will spontaneously follow the addition, while those molecules which are more positive than ammonia add to neutral aldehydes and ketones producing stable hydroxy addition products. For example, methyl and ethyl amines add to formaldehyde, giving $H-C\begin{matrix}O-H\\NHCH_3\end{matrix}$ and $HC\begin{matrix}O-H\\NHC_2H_5\end{matrix}$.

Hence we may state the following general principle:

Neutral aldehydes or ketones will add ammonia or substituted ammonias, by one of the carbonyl unions breaking, thus liberating a free bond on the oxygen and carbon. The ammonia hydrogen adds to the oxygen and the amine residue to carbon through nitrogen. If the substituted ammonia is less positive than ammonia, the addition product will dehydrate, giving a double union between the carbonyl carbon and the ammonia nitrogen. In other words, it is the aldehyde (ketone) ion, $>C\begin{matrix}O(-)\\(+)\end{matrix}$, which is the chemically active form of aldehydes and ketones and to it the ammonias add.

It is interesting to note that when two positive amine groups (ϕ = 211.4) unite, one becomes negative while the other remains positive.

[1] For the meaning of ϕ see previous article.

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The fact that the nitrogen atoms have different polarity is proven from the ionization constants of ammonia and hydrazine, the former gives $K_b^{25°} = 1.87 \times 10^{-5}$ while for the latter we have $K_b^{25°} = 3 \times 10^{-6}$. From the previous work upon polarity it is evident that the second NH_2 radical in hydrazine behaves as a negative group, since it reduces the ionization of ammonia. The fact that when two like atoms combine one must be positive while the other is negative was first suggested by W. A. Noyes[1] from the reaction between chlorine and ammonia.

In the case of negative aldehydes and ketones, the less positive the substituted ammonia which adds, the more chance that it will give a stable hydroxy addition product. The work of R. S. Curtiss[2] upon the substituted amine addition products of dimethyl mesoxalate bears out this deduction. He has been able to isolate in the hydroxyl form addition products of the above ester with aniline ($\phi = 107$) and urea ($\phi = 72.2$), while attempts to isolate a similar compound with ammonia ($\phi = 211.4$) have failed.

Similarly, with aldehydes and ketones possessing an excess of positivity within the molecule, it should be easier to isolate the hydroxy addition products of substituted ammonias the more positive the substituted ammonia.

URBANA, ILL.,
April 21, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

APPLICATION OF POLARITY MEASURED IN TERMS OF A LOGARITHMIC FUNCTION OF THE IONIZATION CONSTANT. II. SCALE OF COMBINED INFLUENCE OF SUBSTITUTION IN ORGANIC COMPOUNDS.

BY C. G. DERICK.

Received May 15, 1911.

Michael,[3] following the idea of van't Hoff that the atoms in a molecule act upon each other through direct union (through space) or indirectly through intermediate atoms, states[4] "if we number a certain atom in any fatty compound with a normal carbon chain by the figure 1, our present knowledge of the combined mutual influence between this atom and the others in the molecule is expressed by the following scale of combined influence, the number indicating the degree of removal and the extent of influence decreasing in the order given: 2–3–5–6–4–7–(9–10–11)–8. It is to be strongly emphasized that the effect of any atom in the position 2 or 3 is *far greater* than that of any similar atom less closely connected,

[1] THIS JOURNAL, 23, 460 (1901).
[2] *Ibid.*, 31, 1053 (1909).
[3] *J. prakt. Chem.*, [2] 60, 331; *Ber.*, 39, 2138, 2780; 40, 141.
[4] THIS JOURNAL, 32, 999 (1910).

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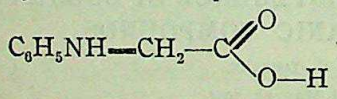
and in the case of atoms farther removed, the influence must be largely direct (*i. e.*, spatial)."

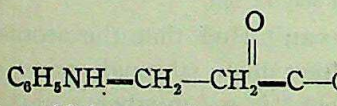
B. Flürscheim[1] has also studied the effect of substitution of radicals into a molecule upon a given atom. He attributes this effect to three factors: polarity of the substituent, the amount of affinity which the substituent requires (the quantitative factor), and stearic hindrance. Not having an accurate measure of these factors, he arbitrarily assigns them certain values and then proceeds to test his hypotheses, which he illustrates thus: "If we have, for example, an unsaturated atom (or group) substituting hydrogen in the α-position the carbon atom will be more strongly bound by it; this leads to a reduction of the force with which the α-(carbon) atom binds the carbonyl carbon atom, to a stronger linking between the latter and oxygen and therefore to a weakening of the bond between oxygen and hydrogen. The following examples illustrate this case. Although aniline is a base, anilinoacetic acid (K = 0.000038) is stronger than acetic acid (K = 0.0000186).

"On the other hand, an unsaturated atom substituting hydrogen in the β-position must have exactly the opposit effect—it takes up a greater amount of the affinity of the β-carbon than does hydrogen; the amount of affinity with which the β-carbon can bind the α-carbon is thereby lessened and the strength of the linking between the latter and the carbonyl carbon is increased. That between the latter and oxygen diminished, and the bond between oxygen and hydrogen is strengthened. β-Anilinopropionic acid (k = 0.000004) is weaker than propionic acid (k = 0.000013)."

Graphically, he would represent the above facts as follows:



Anilinoacetic acid.



β-Anilinopropionic acid.

The relative thickness of the bonds shows, qualitatively, the relative strength of the union. He assumes that weak chemical union favors ionizations.

It is interesting to note that he did not test these conclusions beyond the β-position in the above case. According to his theory γ-anilino substituted acids should have K_a greater than K_a for the β-isomers. He calls the halogens "unsaturated" atoms and shows how, in the case of the *o*-, *m*-, and *p*-halogen benzoic acids, his theory applies. Yet reference to Table II will show that it does not hold in a single case for the halogen-substituted open-chain acids. He overlooks the fact that radicals

[1] *J. Chem. Soc.*, 95, 718 (1909).

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are amphoteric by confusing this property with his quantitative factor. The illustrations are the exception rather than the rule. Finally Flürscheim needlessly confuses the problem. The direct and indirect influences

TABLE I.—A LOGARITHMIC FUNCTION OF THE IONIZATION CONSTANT AS A MEASURE OF THE DIRECT AND INDIRECT INFLUENCES OF RADICALS UPON THE MOLECULE.

Name.[1]	$K^{25°}$.	Log K.—1000/Log. K.	
cis-α,α′-Methylallylsuccinic acid	$2.33\ 10^{-4}$	—3.632	275.2
trans-α,α′-Methylallylsuccinic acid	$2.43\ 10^{-4}$	—3.613	277.0
cis-α,α′-Ethylallylsuccinic acid	$3.59\ 10^{-4}$	—3.444	290.4
trans-α,α′-Ethylallylsuccinic acid	$2.69\ 10^{-4}$	—3.569	280.0
cis-α,α′-Dimethylsuccinic acid	$1.24\ 10^{-4}$	—3.906	256.0
trans-α,α′-Dimethylsuccinic acid	$1.93\ 10^{-4}$	—3.714	269.0
Methyl *cis*-α,α′-dimethylsuccinate	$4.55\ 10^{-5}$	—4.341	219.7
Methyl *trans*-α,α′-dimethylsuccinate	$6.05\ 10^{-5}$	—4.217	237.3
cis-α,α′-Diethylsuccinic acid	$2.01\ 10^{-4}$	—3.696	270.5
trans-α,α′-Diethylsuccinic acid	$2.45\ 10^{-4}$	—3.611	277.0
cis-α,α′-Dipropylsuccinic acid	$4.9\ 10^{-4}$	—3.308	302.0
trans-α,α′-Dipropylsuccinic acid	$2.5\ 19^{-4}$	—3.602	277.7
cis-α,α′-Diisopropylsuccinic acid	$2.3\ 10^{-3}$(?)	—2.637(?)	379.0(?)
trans-α,α′-Diisopropylsuccinic acid	$1.08\ 10^{-4}$	—3.966	250.0
Methyl *cis*-α,α′-diisopropylsuccinate	$1.15\ 10^{-4}$	—3.938	254.0
Methyl *trans*-α,α′-diisopropylsuccinate	$1.24\ 10^{-4}$	—3.906	256.0
cis-α,α′-Dimethylglutaric acid	$5.2\ 10^{-4}$	—4.283	233.5
trans-α,α′-Dimethylglutaric acid	$5.9\ 10^{-4}$	—4.228	236.5
cis-β-Methylglutaric acid	$1.29\ 10^{-4}$	—3.888	257.8
trans-β-Methylglutaric acid	$1.39\ 10^{-4}$	—3.856	259.2
cis-α,γ-Tricarballylic acid	$5.45\ 10^{-4}$	—3.262	306.5
trans-α,γ-Tricarballylic acid	$4.45\ 10^{-4}$	—3.351	298.0
Maleic acid	$1.2\ 10^{-2}$	—1.921	521.0
Fumaric acid	$9.0\ 10^{-4}$	—3.044	328.4
cis-Hexahydroterephthalic acid	$3.0\ 10^{-5}$	—4.523	221.0
trans-Hexahydroterephthalic acid	$4.56\ 19^{-5}$	—4.341	230.4
cis-Hexahydrophthalic acid	$4.4\ 10^{-5}$	—4.356	229.7
trans-Hexahydrophthalic acid	$6.2\ 10^{-5}$	—4.207	237.8
cis-Pentamethylenedicarboxylic acid (1,2)	$1.58\ 10^{-4}$	—3.801	263.2
trans-Pentamethylenedicarboxylic and (1,2)	$1.16\ 10^{-4}$	—3.936	253.7
cis-Pentamethylenedicarboxylic acid (1,3)	$5.4\ 10^{-5}$	—4.267	234.2
trans-Pentamethylenedicarboxylic acid (1,3)	$5.0\ 10^{-5}$	—4.301	231.6
cis-Tetramethylenedicarboxylic acid (1,2)	$6.6\ 10^{-5}$	—4.179	239.0
trans-Tetramethylenedicarboxylic acid (1,2)	$2.8\ 10^{-5}$	—4.552	219.7
cis-Trimethylenedicarboxylic acid (1,2)	$4.0\ 10^{-4}$	—3.399	294.0
trans-Trimethylenedicarboxylic acid (1,2)	$2.06\ 10^{-4}$	—3.686	271.2
trans-Tartaric acids:			
d-Tartaric acid	$9.7\ 10^{-4}$	—3.012	331.8
l-Tartaric acid	$9.7\ 10^{-4}$	—3.012	331.8
r-Tartaric acid	$9.7\ 10^{-4}$	—3.012	331.8
cis-Tartaric acid (i) (*meso*) Tartaric acid	$6.0\ 10^{-4}$	—3.221	310.4

[1] In this table *cis* refers to *cis*-form of geometric isomers or to *meso*-form of optical isomers. Similarly *trans* refers to *trans*-form of geometric isomers or *d*, *l* and *r* optical isomers.

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mentioned by van't Hoff are sufficient to account for all the phenomena the former mentions. Flürscheim's quantitative factor is a confusion of the amphoteric nature of radicals with van't Hoff's indirect factor of influence. The stearic hindrance factor fails to include the full meaning of the direct spatial factor as van't Hoff stated it. Lack of a quantitative measure of the factors under discussion has led both Michael and Flürscheim to wrong conclusions, as will be developed more fully later.

The question immediately suggests itself, What shall be a measure of these influences? Table I shows that —1000/logarithm of K may be taken as such a measure. (Polarity as defined in the last paper = — 1000/log K.) The table shows clearly that the ionization constant will measure, relatively, the combined influence of the direct and indirect factors of a substituent upon the rest of the molecule as expressed in the given group which ionizes. For example, in each case of *cis-trans*-isomerism of the unsaturated dicarboxylic acids, the same number and kinds of atoms intervene between the carboxyl radicals of each isomer, so that if the ionization constant was not affected by the direct space influence of atoms, each isomer ought to have the same ionization constant *due to the same indirect influence*. Table I shows that this is not the case, nor has a single example been found in which the *cis* and *trans* isomers have the same ionization constant. Hence the difference in the ionization constants of *cis* and *trans* isomers must be attributed to the direct space influence of the radical, as Ostwald first noted. It becomes clear, therefore, *that some function of the ionization constant may be taken as a relative measure of the combined direct and indirect influences of radicals upon a given atom or molecule.*

Since each atom in the molecule exerts a direct and indirect influence upon the ionization, as Table II will show, the ionization constant for a given ionizing group expresses the resultant of the combined influence of the direct and indirect factors of every atom in the molecule. Table II will show that the combined influence of hydrogen or an alkyl radical is very small, and their substitution into a given molecule has little effect upon the ionization and therefore their combined influence (direct and indirect) is very small. (See the paraffin monocarboxylic acid and their monoolefin derivatives No. B and No. A, I). In the case of the other atoms the combined direct and indirect influences may be very great (see paraffin dicarboxylic acids). To determine the combined influence of the direct and indirect factors for a given radical, we must substitute it into a given acid and note the effect in the change of the ionization constant. Since the ionization constant of the unsubstituted acid expresses the combined influence of all the atoms in the molecule, the change in the ionization constant produced by substituting a given group for hydrogen will express the value of the combined direct and indirect

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influences of the substituent. By varying the position of the substituent with reference to the ionizing group the combined direct and indirect influences of the substituent with reference to the ionizing group may be determined. A correction for the hydrogen displaced should be applied, but since it is so small it may be safely neglected without appreciably changing the relative results desired.

The method of application of this measure of the scale of combined influence of the direct and indirect influence of substituents will be illustrated by the following. Supposing it is desired to test the relative scale of combined influence for chlorine when substituted in different positions of a normal fatty acid, say butyric acid. In Table II (No. A, II, III, and IV) will be found the logarithms of the ionization constants for butyric and the chloro-substituted butyric acids. First determin the ratio of the combined direct and indirect influences of the atoms in the substituted and unsubstituted acids, thus α-chlorobutyric acid: butyric acid = —1000/log K (α-chlorobutyric): —1000/log K (butyric) = log K (butyric)/log K (α-chlorobutyric) = —4.807/—2.857 = 1.682/1.

β-Chlorobutyric acid: butyric acid = (—4.807) : (—4.049) = 1.186 : 1

γ-Chlorobutyric acid: butyric acid = (—4.807) : (—4.523) = 1.062 : 1

δ-Chlorobutyric acid: valerianic acid = (—4.796) : (—4.690) = 1.022 : 1

Subtracting the combined influence of the other atoms in the molecule (which is equal to the logarithm of the ionization constant of butyric acid and equal to one in the above ratio, neglecting the effect of the displaced hydrogen) we have:

$$\alpha\text{-factor} = 1.682 - 1 = 0.682$$
$$\beta\text{-factor} = 1.186 - 1 = 0.187$$
$$\gamma\text{-factor} = 1.062 - 1 = 0.062$$
$$\delta\text{-factor} = 1.022 - 1 = 0.022$$

Therefore the relative scale of the combined direct and indirect actions of chlorine in the α-, β-, γ- and δ-positions as measured by the carboxyl group in the α-position is:

$$\alpha : \beta : \gamma : \delta = 0.682 : 0.186 : 0.062 : 0.022^{1}$$

Thus it is evident that the scale for the combined influence for a given radical may be measured for at least one type of chemical reaction and Michael's "scale of combined influence" may be tested as well as the conclusions drawn by Flürscheim.

To understand Michael's scale of combined influence it is better to translate his nomenclature into that commonly employed by the organic chemist. One illustration will suffice to show the relation, namely, γ-bromocaproic acid:

[1] The regularity in these ratios will be treated later.

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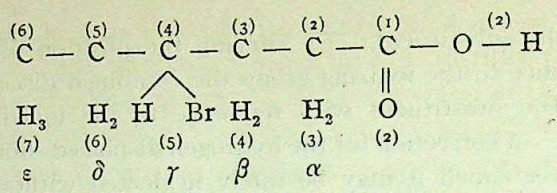

Thus in the γ-position, the carbon is in position (4) and the bromine in position (5) with respect to the carbonyl carbon in position (1). In Table II the first column gives Michael's nomenclature and the last column the factor corresponding to the combined influence of the direct and indirect actions of the given radical for the given position.

It is evident from Tables I and II that no general "scale of combined influence" for all atoms in a molecule upon a given atom can be stated. The order of such a scale of combined influence for water solution is dependent upon polarity as well as external conditions of temperature and pressure. Taking into consideration polarity we may make certain general statements, namely:

1. That in open-chain compounds possessing normal chains, if the substituent is negative then the scale of combined influence for a given negative group in position (1) is 2, 3, 4, 5, 6, 7, 8, 9, etc.; *i. e.*, greatest when the negative substituent is in position 2 and decreases, proportional to the number of carbon atoms intervening. For example, the scale of combined influence for chlorine as measured by the carboxyl group in position (1) is $3 : 4 : 5 : 6 = \alpha : \beta : \gamma : \delta = 0.680 : 0.189 : 0.063 : 0.024$. A notable exception to this rule is that of the unsaturated acids containing a double union. The order of influence in this case has been fully developed by the author in a previous paper.[1] In this case the maximum effect is produced in (3) not (2) as in all other cases.

2. That in all cases except where the substituent is of great negativity the effect of the substitution of negative radicals upon a given negative radical in position (1) has fallen to a constant value by the γ-position (5 in the above scale) which is approximately that of the corresponding unsubstituted acid. A slight residual effect is always present so that the ionization of the substituted acid never completely falls to that of the corresponding unsubstituted acid.

3. When the substituent is positive and the group in position (1) is also positive no general rule for the scale of combined influence is possible. However, if both positive groups are amine ($—NH_2$), then the order of influence of one amine group upon the other in position (1) is 2, 3, 4, 5, 6, etc., the minimum effect being in position (2), and the effect increasing as the number of carbon atoms intervening between the amine groups are increased. The case of the dicarboxylic paraffin acids offers the anal-

[1] THIS JOURNAL, 32, 1339 (1910).

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ogous example where both groups are negative and of the same kind, but an exact opposite order of influence is obtained (see tables), the maximum effect being in position (2) and decreasing, proportional to the number of carbon atoms intervening between the two carboxyl groups.

4. That in the case of ring compounds no general scale of combined influence can be stated. In the case of the halogen-substituted benzoic acids, it is interesting to notice that in the ortho position the order of influence of the halogens is Br > I > Cl, while in the meta position Cl > Br > I as in the case of all normal chain halogen acids for the halogens in any similar position. The order of influence of the halogenated benzoic acids is not general for other substituted benzoic acids even though the substituent is more "unsaturated" as Flürscheim would lead us to believe.

5. Michael further states that the effect of any atom in the position 2 or 3 (α) is far greater than that of any similar atom less closely connected, and in the case of atoms farther removed, the influence must be largely direct, *i. e.*, spatial. He implies that the spatial influence of groups is always less than the direct influence of a group in position 3 (α). This is not necessarily true and depends upon the relative negativity or positivity of the substituent. For example, malonic acid has the ionization constant 1.63×10^{-3} at 25°. It has a carboxyl in position 3 (α) which acts mainly indirectly through the α carbon atom upon the other carboxyl group. In furmaric acid $\begin{matrix}(\mathrm{HOOC.CH}\\ \|\\ \mathrm{CH.COOH})\end{matrix}$ we have a carboxyl group in position 4 (β), which acts mainly indirectly through two carbon atoms, doubly bound, upon the carboxyl group in position 1; its ionization constant at 25° is 9×10^{-4}. In the isomeric maleic acid $\begin{matrix}(\mathrm{HOOC—CH}\\ \|\\ \mathrm{HOOC—CH})\end{matrix}$, the same indirect influence is present as in fumaric acid, yet its ionization constant at 25° is 1.2×10^{-2}, due to the greater direct spatial influence of the carboxyl group. But the ionization constant of maleic acid is greater than that of malonic acid in spite of the fact that in the latter the carboxyl group is in position 3 (α). Hence it is evident that the direct spatial influence of a carboxyl group in position 4 (β) may be greater than the indirect influence of the same group in position 3. Again it is evident that no general conclusions as to the "scale of combined influence can be drawn, but a logarithmic function of the ionization constant may be used to determine this scale in any given case under discussion.

6. For other conclusions see "Affinitätmessungen an schwachen Säuren und Basen," by H. Lundén, page 77.

7. Lactone and anhydride formations.

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TABLE II—A. ORDER OF EFFECT OF NEGATIVE SUBSTITUENTS IN A NORMAL ALIPHATIC COMPOUND UPON A GIVEN NEGATIVE RADICAL (CARBOXYL RADICAL).

Name.	Formula.	Ka.	Log K.	Factors.
I. Double Union:				
2[2] Δ^1-Pentenic acid.....	$C_2H_5.CH = CH.CO_2H$	$1.48\ 10^{-5}$	—4.830	—0.007[1]
3 Δ^2-Pentenic acid.....	$CH_3CH = CHCH_2CO_2H$	$3.35\ 10^{-5}$	—4.475	+0.0095
4 Δ^3-Pentenic acid.....	$CH_2 = CH.(CH_2)_2CO_2H$	$2.09\ 10^{-5}$	—4.680	+0.024
2 Δ^1-Hexenic acid.....	$C_3H_7.CH = CHCO_2H$	$1.89\ 10^{-5}$	—4.724	+0.0395
3 Δ^2-Hexenic acid.....	$C_2H_5CH = CH_2CO_2H$	$2.64\ 10^{-5}$	—4.578	+0.057
4 Δ^3-Hexenic acid.....	$CH_3CH = CH(CH_2)_2CO_2H$	$1.74\ 10^{-5}$	—4.758	+0.018
5 Δ^4-Hexenic acid.....	$CH_2 = CH.(CH_2)_3CO_2H$	$1.91\ 10^{-5}$	—4.718	+0.026
II. Chlorine:				
3 α-Chlorobutyric acid...	$C_2H_5CHClCO_2H$	$1.39\ 10^{-3}$	—2.857	0.680
4 β-Chlorobutyric acid....	$CH_3CHOCH_2CO_2H$	$8.94\ 10^{-5}$	—4.049	0.187
5 γ-Chlorobutyric acid....	$CH_2Cl.(CH_2)_2CO_2H$	$3.0\ 10^{-5}$	—4.523	0.063
6 δ-Chlorovalerianic.....	$CH_2Cl(CH_2)_3CO_2H$	$2.04\ 10^{-5}$	—4.690	0.023
III. Bromine:				
3 α-Bromoacetic acid....	$CH_2Br.CO_2H$	$1.38\ 10^{-3}$	—2.860	0.655
4 β-Bromopropionic acid..	$CH_2Br.CH_2CO_2H$	$9.8\ 10^{-5}$	—4.009	0.210
5 γ-Bromobutyric acid ...	$CH_2Br(CH_2)_2CO_2H$	$2.6\ 10^{-5}$	—4.585	0.047
6 δ-Bromovalerianic acid.	$CH_2Br(CH_2)_3CO_2H$.	$1.91\ 10^{-5}$	—4.719	0.017
IV. Iodine:				
3 α-Iodoacetic acid.....	CH_2ICO_2H	$7.5\ 10^{-4}$	—3.125	0.515
4 β-Iodopropionic acid...	$CH_2ICH_2OCO_2H$	$9.0\ 10^{-5}$	—4.046	0.167
5 γ-Iodobutyric acid.....	$CH_2I(CH_2)_2CO_2H$	$2.3\ 10^{-5}$	—4.638	0.035
6 δ-Iodovalerianic acid...	$CH_2I(CH_2)_3CO_2H$	$1.71\ 10^{-5}$	—4.767	0.008

[1] A minus value for these factors mean that the substituting group decreases the hydrogen ionization of the unsubstituted acid instead of increasing the same. These calculations were made using the slide rule, but are accurate enough for the purpose of this article.

[2] The column refers to the nomenclature used by Michael.

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V. *Hydroxyl:*				
3 α-Hydroxyacetic	CH_2OHCO_2H	$1.5\ 10^{-4}$	—3.824	0.238
4 β-Hydroxypropionic ...	$CH_2OH.CH_2CO_2H$	$3.1\ 10^{-5}$	—4.509	0.073
5 γ-Hydroxybutyric acid.	$CH_2OH.(CH_2)CO_2H$	$1.93\ 10^{-5}$	—4.714	0.018
VI. Carboxyl.				
2 Oxalic acid	HOOC.COOH	$1.00\ 10^{-1}$	—1.000	2.670
3 Carboxyacetic acid.....	$HO_2CCH_2CO_2H$	$1.64\ 10^{-3}$	—2.785	0.710
4 β Carboxypropionic acid	$HO_2C(CH_2)_2CO_2H$	$6.7\ 10^{-5}$	—4.174	0.160
5 γ-Carboxybutyric acid..	$HO_2C(CH_2)_3CO_2H$	$4.7\ 10^{-5}$	—4.328	0.111
6 δ-Carboxyvalerianic acid	$HO_2C(CH_2)_4CO_2H$	$3.7\ 10^{-5}$	—4.432	0.083
7 ε-Carboxycaproic acid..	$HO_2C(CH_2)_5CO_2H$	$3.23\ 10^{-5}$	—4.491	0.076
8 ζ-Carboxyeonanthic acid	$HO_2C(CH_2)_6CO_2H$	$2.99\ 10^{-5}$	—4.524	0.069
9 η-Carboxycaprylic acid..	$HO_2C(CH_2)_7CO_2H$	$2.5\ 10^{-5}$	—4.602	0.053
10 θ-Carboxypelargonic acid	$HO_2C(CH_2)_8CO_2H$	$2.38\ 10^{-5}$	—4.624	0.072
VII. Carboxyethyl.				
3 Carboxyethylacetic acid.	$C_2H_5OOC.CH_2CO_2OH$	$4.51\ 10^{-4}$	—3.346	0.407
4 β-Carboxyethylpropionic	$C_2H_5O_2C.(CH_2)_2CO_2H$	$3.02\ 10^{-5}$	—4.520	0.072
8 ζ-Carboxyethyleonanthic	$C_2H_5O_2C(CH_2)_6CO_2H$	$1.46\ 10^{-5}$	—4.836	0.000
10 θ-Carboxyethylpelargonic	$C_2H_5O_2C(CH_2)_8CO_2H$	$1.43\ 10^{-5}$	—4.845	—0.003
VIII. Phenyl.				
3 Phenylacetic acid.....	$C_6H_5CH_2CO_2H$	$5.02\ 10^{-5}$	—4.276	0.107
4 β-Phenylpropionic acid.	$C_6H_5(CH_2)_2CO_2H$	$2.3\ 10^{-5}$	—4.637	0.043

B.—ORDER OF EFFECT OF POSITIVE SUBSTITUENTS IN A NORMAL ALIPHATIC COMPOUND UPON A GIVEN NEGATIVE RADICAL (CARBOXYL GROUP).

I. Methyl.				
2 Methylformic acid.....	$CH_3.CO_2H$	$1.86\ 10^{-5}$	—4.731	—0.226
3 Methylacetic acid.....	$CH_3CH_2CO_2H$	$1.45\ 10^{-5}$	—4.839	—0.022
3 α-Methylpropionic acid.	$CH_3CH(CH_3)CO_2H$	$1.60\ 10^{-5}$	—4.796	+0.008
4 β-Methylbutyric acid...	$CH_3.CH(CH_3).CH_2CO_2H$	$1.70\ 10^{-5}$	—4.770	+0.006
5 γ-Methylvalerianic acid.	$CH_3CH(CH_3)_2CO_2H$	$1.44\ 10^{-5}$	—4.842	—0.015
1 Methylformic acid.....	CH_3COOH	$1.86\ 10^{-5}$	—4.731	—0.226

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TABLE II (*Continued*).

Name.	Formula.	Ka.	Log K.	Factors.
3 Methylacetic acid.....	$CH_3CH_2CO_2H$	$1.45\ 10^{-5}$	—4.839	—0.022
4 β-Methylpropionic acid.	$CH_3(CH_2)_2CO_2H$	$1.56\ 10^{-5}$	—4.807	—0.004
5 γ-Methylbutyric acid...	$CH_3(CH_2)_3CO_2H$	$1.60\ 10^{-5}$	—4.796	0.000
6 δ-Methylvalerianic acid	$CH_3(CH_2)_4CO_2H$	$1.45\ 10^{-5}$	—4.839	0.000
7 ε-Methylcaproic acid....	$CH_3(CH_2)_5CO_2H$	$1.46\ 10^{-5}$	—4.842	—0.001
8 ζ-Methyleonanthic acid.	$CH_3(CH_2)_6CO_2H$	$1.44\ 10^{-5}$	—4.951	—0.024

C.—ORDER OF EFFECT OF NEGATIVE SUBSTITUENTS IN A NORMAL ALIPHATIC COMPOUND UPON A GIVEN POSITIVE RADICAL (AMINE GROUP).

		K_b		
I. Phenyl:				
2 Phenylamine.....	$C_6H_5NH_2$	$4.6\ 10^{-10}$	—9.337	—0.4935
3 Phenylmethylamine....	$C_6H_5CH_2NH_2$	$2.4\ 10^{-5}$	—4.619	—0.2849

D.—ORDER OF EFFECT OF POSITIVE SUBSTITUENTS IN A NORMAL ALIPHATIC COMPOUND UPON A GIVEN POSITIVE RADICAL (AMINE GROUP).

		K_b		
I. Amine:[1]				
2 Hydrazine.....	NH_2–NH_2(NH_2–NH_3OH)	$3.\ 10^{-6}$	—5.523	—0.144
4 β-aminoethylamine.....	NH_2–$CH_2CH_2NH_2$	$8.5\ 10^{-5}$	—4.071	—0.202
5 γ-aminopropylamine....	$NH_2(CH_2)_3NH_2$	$3.5\ 10^{-4}$	—3.456	—0.028
6 δ-aminobutylamine.....	$NH_2(CH_2)_4NH_2$	$5.1\ 10^{-4}$	—3.293	...
7 ε-aminopentylamine....	$NH_2(CH_2)_5NH_2$	$7.3\ 10^{-4}$	—3.137	...
II. Methyl:				
2 Methylamine.....	CH_3NH_2	$5.0\ 10^{-4}$	—3.301	0.433
3 α-Methylethylamine....	$CH_3CH(CH_3)NH_2$	$5.3\ 10^{-4}$	—3.276	—0.008
4 β-Methylpropylamine...	$CH_3CH(CH_3)CH_2NH_2$	$3.1\ 10^{-4}$	—3.509	—0.052

E.—ORDER OF EFFECT OF NEGATIVE SUBSTITUENTS UPON A GIVEN NEGATIVE RADICAL (CARBOXYL GROUP) IN THE RING.

		K_a		
I. Double union:				
2 Δ^1-Tetrahydrobenzoic acid	$CH_2.CH_2.CH_2.CH = C.COOH$	$2.21\ 10^{-5}$	—4.656	—0.107
3 Δ^2-Tetrahydrobenzoic acid	$CH_2CH_2.CH_2CH = CH.C—COOH$	$3.05\ 10^{-5}$	—4.516	—0.079

[1] Amine substituent is apparently functionating with its amphoteric negative nature until ε-amino pentylamine.

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II. Chlorine:				
4 σ-Chlorobenzoic acid....	CH = CH — CH = CH.C(Cl) = C.COOH	$1.32\ 10^{-3}$	—2.880	0.445
5 *m*-Chlorobenzoic acid...	CH = CH.CH = C(Cl).CH = CCOOH	$1.55\ 10^{-3}$	—2.810	0.480
6 *p*-Chlorobenzoic acid....	CH = CH.C(Cl) = CHCH = CCOOH	$9.3\ 10^{-5}$	—4.032	0.03
III. Bromine:				
4 σ-Bromobenzoic acid...	CH = CH.CH = CH.C(Br) = C.COOH	$1.45\ 10^{-3}$	—2.839	0.466
5 *m*-Bromobenzoic acid..	CH = CH.CH = C(Br).CH = C.COOH	$1.37\ 10^{-3}$	—2.863	0.452
6 *p*-Bromobenzoic acid...	CH = CH.C (Br) = CH.CH = C.COOH	...	.....	.....
IV. Iodine:				
4 σ-Iodobenzoic acid.....	CH = CH — CH = CH.C(I) = C COOH	$1.37\ 10^{-3}$	—2.863	0.452
m-Iodobenzoic acid....	CH = CH.CH = C(I).CH = C.COOH	$1.6\ 10^{-4}$	—3.796	0.05
V. Hydroxyl:				
4 σ-Hydroxybenzoic acid.	CH = CH.CH = CH.C(OH) = C .COOH	$1.04\ 10^{-3}$	—2.983	0.394
5 *m*-Hydroxybenzoic acid	CH = CH.CH = C(CH).CH = C COOH	$8.33\ 10^{-5}$	—4.079	0.018
6 *p*-Hydroxybenzoic acid.	CH = CH.C(OH) = CH.CH = C COOH	$2.9\ 10^{-5}$	—4.538	—0.103
VI. Carboxyl:				
4 σ-Carboxybenzoic acid.	CH = CH.CH = CH.C(CO_2H) = CCO_2H	$1.21\ 10^{-3}$	—2.917	0.425
5 *m*-Carboxybenzoic acid	CH = CH.CH = C(CO_2H).CH = CCO_2H	$2.9\ 10^{-4}$	—3.462	0.176

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TABLE II (*Continued*).

Name.	Formula.	Ka.	Log K.	Factors.
6 *p*-Carboxybenzoic acid..	$CH = CH.CH(CO_2H) = CH.CH = CCO_2H$	$1.5\ 10^{-4}$	—3.398	0.087
VII. Nitro.				
4 *σ*-Nitrobenzoic acid.....	$CH = CH.CH = CH.C(NO_2) = C.CO_2H$	$6.3\ 10^{-3}$	—2.199	0.892
5 *m*-Nitrobenzoic acid....	$CH = CH.CH = C(NO_2)CH = C\ CO_2H$	$3.45\ 10^{-4}$	—3.462	0.201
6 *p*-Nitrobenzoic acid....	$CH = CH.C(NO_2) = CH.CH = CCO_2H$	$4.0\ 10^{-4}$	—3.398	0.224
E.—ORDER OF EFFECT OF POSITIVE SUBSTITUENTS UPON A GIVEN NEGATIVE RADICAL (CARBOXYL GROUP) IN THE RING.				
I. Amine.		K_a		
4 *σ*-Aminobenzoic acid....	$CH = CH.CH : CH.C(NH_2) : C.CO_2H$	$1.06\ 10^{-5}$	—4.975	—0.164
5 *m*-Aminobenzoic acid...	$CH : CH.CH : C(NH_2).CH : C.CO_2H$	$1.63\ 10^{-5}$	—4.788	—0.132
6 *p*-Aminobenzoic acid...	$CH = CH.C(NH_2) = CH.CH = C.CO_2H$	$1.21\ 10^{-5}$	—4.917	—0.123
or				
4 *σ*-Anilinosulfonic acid...	$CH = CH.CH = CH.C(NH_2) = C.SO_3H$	$3.3\ 10^{-3}$	—2.482	...
5 *m*-Anilinosulfonic acid.	$CH = CH.CH = C(NH_2).CH = C.SO_3H$	$1.85\ 10^{-4}$	—3.733	...
6 *p*-Anilinosulfonic acid..	$CH = CH.C(NH_2) = CH.CH = C.SO_3H$	$5.81\ 10^{-4}$	—3.318	...
II. (*N*)-Methylamine:				
4 (*N*)-Methyl-*o*-aminobenzoic acid.....	$CH = CH.CH = CH.C(NHCH_3) = C\ CO_2H$	$4.6\ 10^{-6}$	—5.337	—0.222
5 (*N*)-Methyl-*m*-aminobenzoic acid.....	$CH = CH.CH = C(NHCH_3).CH = CCO_2H$	$8.0\ 10^{-6}$	—5.196	—0.200

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6 (*N*)-Methyl -*p*-aminobenzoic acid	CH = CH.C(NHCH$_3$) = CH.CH = C.CO$_2$H	9.2 10^{-6}	—5.036	—0.175
III. Dimethylamine:				
4 (*N*)-Dimethyl-*o*-aminobenzoic acid.....	CH = CH.CH = CH.C[N(CH$_3$)$_2$] = C.CO$_2$H	2.1 10^{-9}	—8.678	—0.521
5 (*N*)-Dimethyl-*m*-aminobenzoic acid.....	CH = CH.CH = C[N(CH$_3$)$_2$].CH = C.CO$_2$H	8.0 10^{-6}	—5.096	—0.184
6 (*N*)-Dimethyl-*p*-aminobenzoic acid.....	CH = CH.C[N(CH$_3$)$_2$] = CH.CH = C.CO$_2$H	9.4 10^{-6}	—5.027	—0.173
IV Methyl:				
4 *o*-Toluic acid.....	CH = CH.CH = CH.C(CH$_3$) = C.CO$_2$H	1.25 10^{-4}	—3.903	0.065
5 *m*-Toluic acid.....	CH = CH.CH = C(CH$_3$).CH = C.CO$_2$H	5.1 10^{-5}	—4.293	—0.033
6 *p*-Toluic acid.....	CH = CH.C(CH$_3$) = CH.CH = C.CO$_2$H	5.1 10^{-5}	—4.293	—0.033
V. Ring *N*:				
4 α-Pyridine carboxylic acid	CH = CH.CH = CH.C(CO$_2$H) = N	3.0 10^{-6}	—5.522	—0.248
5 β-Pyridine carboxylic acid	CH = CH.CH = C(CO$_2$H.CH = N	1.4 10^{-5}	—4.852	—0.144
6 γ-Pyridine carboxylic acid	CH = CH.C(CO$_2$H) = CH.CH = N	1.1 10^{-5}	—4.959	—0.161

F.—Order of Effect of Negative Substituents upon a Given Positive Radical (Amine Group) in the Ring.

		K_b		
I. Carboxyl:				
4 *o*-Aminobenzoic acid....	CH = CH.CH = CH.C(CO$_2$H) = C.NH$_2$	1.38 10^{-12}	—11.860	—0.213
5 *m*-Aminobenzoic acid...	CH = CH.CH = C(CO$_2$H).CH = C.NH$_2$	1.22 10^{-1}	—10.913	—0.144
4 (*N*)-Methyl *o*-aminobenzoic acid.....	CH = CH.CH = CH–C(CO$_2$H) = C.NHCH$_3$	8.55 10^{-13}	—11.632	—0.326

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TABLE II (*Continued*).

Name.	Formula.	Ka.	Log K.	Factors.
6 *p*-Aminobenzoic acid..	$CH = CH.C(CO_2H) = CH.CH = C.NH_2$	$2.33\ 10^{-12}$	—12.068	—0.197
5 (*N*)-Methyl-*o*-aminobenzoic acid.....	$CH = CH.CH = C(CO_2H).CH = C.NHCH_3$	$1.10\ 10^{-11}$	—10.959	—0.258
6 (*N*)-Methyl-*p*-aminobenzoic acid.....	$CH = CH.C(CO_2H) = CH.CH = C.NHCH_3$	$1.52\ 10^{-12}$	—11.818	—0.312
II. Nitro:				
4 *ε*-Nitraniline.....	$CH = CHCH = CH.C(NO_2) = C.NH_2$	$1.0\ 10^{-14}$	—14.000	—0.333
5 *m*-Nitraniline.....	$CH = CH.CH = C(NO_2.CH = C.NH_2$	$4.0\ 10^{-12}$	—11.398	—0.180
6 *p*-Nitraniline.....	$CH = CH.C(NO_2) = CH.CH = C.NH_2$	$1.0\ 10^{-12}$	—12.000	—0.222

G.—ORDER OF EFFECT OF POSITIVE SUBSTITUENTS UPON A GIVEN POSITIVE RADICAL (AMINE GROUP AND RING NITROGEN) IN THE RING.

I. Methyl:				
4 *ε*-Toluidine.....	$CH = CH.CH = CH.C(CH_3) = C.NH_2$	$3.3\ 10^{-10}$	—9.482	—0.016
5 *m*-Toluidine.....	$CH = CH.CH = C(CH_3).CH = C.NH_2$	$6.0\ 10^{-10}$	—9.222	+0.013
6 *p*-Toluidine.....	$CH = CH.C(NH_3) = CH.CH = C.NH_2$	$2.0\ 10^{-9}$	—8.699	+0.073
4 *α*-Picoline.....	$CH = CH.CH = CH.C(CH_3) = N$	$3.0\ 10^{-8}$	—7.523	0.147
5 *β*-Picoline.....	$CH = CH.CH = C(CH_3).CH = N$	$1.0\ 10^{-8}$	—8.000	0.079
6 *γ*-Picoline.....	$CH = CH.C(CH_3) = CH.CH = N$	$1.0\ 10^{-8}$	—8.000	0.079

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Michael[1] finds the best support of his "scale of combined influence," (1)–2–3–5–6–4–7(9–10–11)–8, in lactone and anhydride formations. He attributes the cause of the same to the fact that halogen, hydroxyl or carboxyl attached to the γ- or δ-carbon exerts a greater space or direct action upon the α-carboxyl then when the same radicals are attached to the β, ε, ζ, η, etc., carbons. Therefore in his "scale of combined influence" positions 5 and 6 are of greater influence than 4, 7 (9–10–11) and 8.

In Table I it was shown that a logarithmic function of K could be used as a measure of this direct influence of radicals as well as of their indirect influence. If this is true, the ionization constants of the γ- or δ-halogen, hydroxyl or carboxyl substituted normal monobasic paraffin acids should be greater than that of the β-substituted isomeric acids. This must be true unless the excess of indirect influence of the β-position over that of the same substituent in the γ- and δ-position is sufficiently great to compensate for the greater direct influence of the latter position which Michael assumes. In Table II will be found the factors of combined influence (direct or indirect) by which the conclusions drawn by Michael may be tested. The combined influence of the direct and indirect actions of halogen, hydroxyl and carboxyl radicals for β-, γ-, and δ-positions (4, 5 and 6 in terms of nomenclature employed by Michael) are as follows:

Chlorine $\beta : \gamma : \delta = 0.187 : 0.063 : 0.023$
Bromine $\beta : \gamma : \delta = 0.210 : 0.047 : 0.017$
Iodine $\beta : \gamma : \delta = 0.167 : 0.035 : 0.008$
Hydroxyl $\beta : \gamma : \delta = 0.073 : 0.018 : \ldots.$
Carboxyl $\beta : \gamma : \delta = 0.160 : 0.111 : 0.083$

In no case, is the combined influence of the direct and indirect actions for these groups less in the β-position than in either the γ- or δ-. This is opposite to the conclusions drawn by Michael. Obviously, we must look further for the reason of lactone and anhydride formations in the paraffin series.

[Contribution from the Chemical Laboratory of the University of Illinois.]

APPLICATION OF POLARITY MEASURED IN TERMS OF A LOGARITHMIC FUNCTION OF THE IONIZATION CONSTANT. III. CORRELATION OF CHEMICAL STRUCTURE WITH IONIZATION.

By C. G. Derick.

Received May 17, 1911.

A. Determination of Structure from Ionization.

Many attempts have been made to use the ionization constant to determine the structure of organic compounds. Many interesting conclu-

[1] *J. prakt. Chem.*, [2] 60, 335 (1899).

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sions have been drawn from isolated cases,[1] but no general connection between the chemical structure of organic electrolytes and their ionization has been found. It is the purpose of this paper to prove that such relationship exists, and that it is of the simplest possible nature for the negative substituted paraffin acids.

When the "scale of combined influence"[2] for a negative substituent upon a carboxyl group in position (1) is 2, 3, 4, 5, 6, 7, 8, 9, 10, etc., the position of the substituent may be predicted if the ionization constant of the substituted and unsubstituted acids together with that of any similar α-substituted paraffin monocarboxylic acid is known. For example the "scale of combined influence" for chlorine in the monobasic paraffin acids upon the carboxyl group in position (1) is found from the following data:

		K_a.	Log K.	Factor.
3	α-Chlorobutyric acid, $C_2H_5CHClCO_2H$.....	1.39×10^{-3}	—2.857	0.6825
4	β-Chlorobutyric acid, $CH_3CHClCH_2CO_2H$..	8.94×10^{-5}	—4.049	0.1873
5	γ-Chlorobutyric acid, $CH_2Cl(CH_2)_2CO_2H$...	3.0×10^{-5}	—4.523	0.0627
6	δ-Chlorovalerianic acid, $CH_2Cl(CH_2)_3CO_2H$.	2.04×10^{-7}	—4.690	0.0229

From this it is evident that the scale for combined influence for chlorine in the monobasic paraffin acids upon the carboxyl groups in position (1) is:

$$\alpha : \beta : \gamma : \delta \text{ (or } 3 : 4 : 5 : 6) = 0.6825 : 0.1873 : 0.0627 : 0.0229$$

If we call the α-factor one we have:

$$\alpha : \beta : \gamma : \delta, \text{ etc.}, = 1 : {}^1/_3 : {}^1/_9 : {}^1/_{27}, \text{ etc.}$$

In other words the effect of substituting chlorine in the β-position is about $^1/_3$ of that in the α-position, similarly that of the γ-position $^1/_9$ and that of the δ-position $^1/_{27}$. The fact that the α-place factor for chlorine is slightly greater than three times the β-factor is due in part to the fact that α-chlorbutyric is a fairly strong electrolyte and tends to deviate a little from the mass law by which the calculations were made. Or it may be due to inaccuracy in the determination of the constant. This fact, however, will not influence the accuracy with which structure may be determined, as will be seen later.

As shown in the article on the "Scale of Combined Influence of Substituents in Organic Compounds,"[2] the factors used above are determined as follows: The influence of all the atoms in the molecule upon the carboxyl group in position (1) is defined as proportional to $1/\log K$. It is assumed that this factor is made up additively of the factors of each atom in the molecule. The ratio of these combined influences for the

[1] W. Ostwald, *Z. physik. Chem.*, 3, 170 (1889), in the case of mono and dinitro caproic acids. Also H. Lunden, "Affinitätmessungen an schwachen Säuren und Basen," page 77.

[2] THIS JOURNAL, page 1167.

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substituted acid to that of the unsubstituted acid is determined. To find the combined direct and indirect influences of the substituent for a given position, the combined influences of the rest of the atoms in the molecule are subtracted from the value of the ratio. The combined influence of the rest of the atoms in the molecule is taken equal to unity, thereby neglecting the value for the hydrogen atom replaced, which occurs additively and is a very small value. This result follows from the fact that in the above ratio the influence of all the atoms in the molecule of the unsubstituted acid is unity, since it occurs in the denominator. For example the α-place factor for chlorine in α-chlorobutyric acid is desired. The ionization constants of α-chlorobutyric and butyric acids are 1.39×10^{-3} and 1.56×10^{-5}, respectively. The ratio of the combined influence of all the atoms in the α-chlor acid to those in the unsubstituted butyric acid is

$$\alpha\text{-Chlorobutyric} : \text{Butyric} = 1/\log 1.39 \times 10^{-3} : 1/\log 1.56 \times 10^{-5} = -4.807/-2.857 = 1.6825/1.$$

The combined influences of the direct and indirect actions of chlorine in the α (3) position upon the carboxyl group in position (1) is $1.6825 - 1.0000 = 0.6825$. In other words, the place factor for α-chlorine is 0.6825. Finally the scale of combined influence for chlorine in the above series of chlor acids is:

$$\alpha : \beta : \gamma : \delta, \text{ etc. (or } 3 : 4 : 5 : 6, \text{ etc.)} = 0.6825 : 0.6825/3 : 0.6825/9 : 0.6825/27, \text{ etc.}$$

The question immediately suggests itself, How general is this rule of thirds for the place factors? In the following table will be found the available data to test this rule.

From Table I, it is evident that the rule of thirds is generally applicable. It holds quite accurately for chlorine, bromine, iodine, hydroxyl and phenyl radicals. The fact that it does not hold for a molecule containing two carboxyl groups is to be expected, since the substitution of a second ionizing group must necessarily interfere with the above measure of the direct and indirect actions of substituents. Table I shows that the farther the two carboxyl groups are removed from each other the greater is the deviation, suggesting that both carboxyl groups are ionizing. The effect of the substituents would be thereby magnified. If each carboxyl group is affected the same amount, then the one-third rule should become a two-thirds rule. This is approximately true for glutaric, adipic, and succinic acids, since the place factor for the β-carboxyl group is 0.1594 and $^2/_3$ of the same gives 0.1063, while the measured place factor for γ-carboxyl group is 0.1107 (glutaric acid). This fact in conjunction with the fact that beginning with succinic acid the half-esters of this homologous series give ionization constants just one-

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half of the corresponding free acids, as discovered by J. Walker,[1] is very suggestive.

TABLE I.

Name.	Formula.	Ka.	Log Ka	Factor.
I. Chlorine:				
3[2] or α-Chloroacetic acid...	CH_2ClCO_2H	$1.55\ 10^{-3}$	—2.80967	0.6830
3 α-Chloropropionic acid...	$CH_3CH(Cl)CO_2H$	$1.47\ 10^{-3}$	—2.83268	0.7083
4 β-Chloropropionic acid...	$CH_2ClCH_2CO_2H$	$8.59\ 10^{-5}$	—4.06601	0.1901
3 α-Chlorobutyric acid....	$C_2H_5CHClCO_2H$	$1.39\ 10^{-3}$	—2.85699	0.6826
4 β-Chlorobutyric acid....	$CH_3CHClCH_2CO_2H$	$8.94\ 10^{-5}$	—4.04866	0.1873
5 γ-Chlorobutyric acid.....	$CH_2Cl(CH_2)_2CO_2H$	$3.\ 10^{-5}$	—4.52288	0.0627
6 δ-Chlorovalerianic acid..	$CH_2Cl(CH_2)_3CO_2H$	$2.04\ 10^{-5}$	—4.69037	0.0230
II. Bromine:				
3 Bromoacetic acid.....	CH_2BrCO_2H	$1.38\ 10^{-3}$	—2.86012	0.6539
3 α-Bromopropionic acid..	$CH_3CH.BrCO_2H$	$1.08\ 10^{-3}$	—2.96658	0.6312
4 β-Bromopropionic acid...	$CH_2BrCH_2CO_2H$	$9.8\ 10^{-5}$	—4.00877	0.2071
3 α-Bromobutyric acid....	$C_2H_5CHBrCO_2H$	$1.06\ 10^{-3}$	—2.97469	0.6159
5 γ-Bromobutyric acid....	$CH_2Br(CH_2)_2CO_2H$	$2.6\ 10^{-5}$	—4.58503	0.0484
6 δ-Bromovalerianic acid..	$CH_2Br(CH_2)_3CO_2H$	$1.91\ 10^{-5}$	—4.71897	0.0169
III. Iodine:				
3 Iodoacetic acid.....	CH_2ICO_2H	$7.5\ 10^{-4}$	—3.12494	0.5138
4 β-Iodopropionic acid....	$CH_2ICH_2CO_2H$	$9.\ 10^{-5}$	—4.04576	0.1961
5 γ-Iodobutyric acid.....	$CH_2I(CH_2)_2CO_2H$	$2.3\ 10^{-5}$	—4.63827	0.0363
6 δ-Iodovalerianic acid....	$CH_2I(CH_2)_3CO_2H$	$1.71\ 10^{-5}$	—4.76700	0.0061
IV. Hydroxyl:				
3 Glycolic acid.....	CH_2OHCO_2H	$1.5\ 10^{-4}$	—3.82391	0.2371
3 Lactic acid.....	$CH_3CH(OH)CO_2H$	$1.38\ 10^{-4}$	—3.86012	0.2536
4 β-Hydroxypropionic acid.	$CH_2OHCH_2CO_2H$	$3.1\ 10^{-5}$	—4.50864	0.0733
5 γ-Hydroxybutyric acid...	$CH_2OH(CH_2)_2CO_2H$	$1.93\ 10^{-5}$	—4.71444	0.0196
3 α-Hydroxyisobutyric acid	$(CH_3)_2C(OH)CO_2H$	$1.06\ 10^{-4}$	—3.97469	0.2039
5 γ-Hydroxyvalerianic acid.	$CH_3CHOH(CH_2)_2CO_2H$	$2.0\ 10^{-5}$	—4.69897	0.0214
V. Carboxyl:				
3 Malonic acid.....	$HO_2C.CH_2.CO_2H$	$1.64\ 10^{-3}$	—2.78516	0.6982
4 Succinic acid.....	$HO_2C(CH_2)_2CO_2H$	$6.7\ 10^{-5}$	—4.17393	0.1594
5 Glutaric acid.....	$HO_2C(CH_2)_3CO_2H$	$4.7\ 10^{-5}$	—4.32790	0.1107
6 Adipic acid.....	$HO_2C(CH_2)_4CO_2H$	$3.7\ 10^{-5}$	—4.43180	0.0827
7 Pimelic acid.....	$HO_2C(CH_2)_5CO_2H$	$3.2\ 10^{-5}$	—4.49485	0.0761
VI. Oximido:				
3 α-Oximinoacetic acid (*syn*)	$HON = CH.CO_2H$	$9.95\ 10^{-4}$	—3.00218	0.5756
3 α-Oximinobutyric acid (*syn*)	$HON = C.(C_2H_5)CO_2H$	$8.3\ 10^{-4}$	—3.08092	0.5602
VII. Phenyl:				
3 Phenylacetic acid.....	$C_6H_5CH_2CO_2H$	$5.6\ 10^{-5}$	—4.25181	0.1126
3 α-Phenylpropionic acid..	$C_6H_5CH(CH_3)CO_2H$	$4.3\ 10^{-5}$	—4.36653	0.1082
4 β-Phenylpropionic acid..	$C_6H_5CH_2CH_2CO_2H$	$2.3\ 10^{-5}$	—4.63827	0.0434

A second important conclusion may be drawn from the table. The α-factor is the same for a given substituent, independent of the acid from

[1] *J. Chem. Soc.*, 61, 605 (1892); 67, 147 (1895).

[2] Nomenclature used by Michael, *J. prakt. Chem.*, 60, 324 (1899).

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which it is derived. For example, the α-factors for chlorine as derived from acetic, propionic and butyric acids and their α-chloro- derivatives are 0.6830, 0.7083, and 0.6826 respectively. If we add the influence of the other atoms in the molecule (equals 1) we have 1.6830, 1.7083, and 1.6826, respectively; that is, a difference of about two parts in one hundred and seventy as used in the calculations to follow. The data available show that the above fact holds for the negative substituents chlorine, bromine, hydroxyl, oximido and phenyl.

To determin the position of these radicals in the monobasic paraffin acids, we need only to know the α-factor for the given radical (obtained from any α-substituted monobasic paraffin acid and the corresponding unsubstituted acid) and the ionization constant of the substituted and corresponding unsubstituted acids. This will be illustrated as follows: Analysis and group tests or previous history show that an unknown substance is a bromopropionic acid. Its ionization constant is determined to be 9.8×10^{-5}, while that of the corresponding unsubstituted acid (propionic) is 1.45×10^{-5}. These two values give the place factor for the bromine in the unknown acid the value 0.2052. From Table I, the best α-place factor is 0.6159. The ratio of the place factors for bromine in the unknown acid to that in the α-brom acid is $0.2052/0.6157 = 0.3332$. Hence bromine is in the β-position in the unknown acid, according to the rule of thirds. From this illustration it is evident that the location of the negative substituent may be determined with certainty for the α-, β-, γ- and δ-positions even though the error in the ionization constants is relatively large, since if we use the α-bromine place factors obtained from acetic and propionic acids, given in Table I, the above ratio gives the values 0.3137 and 0.3102. There can be no doubt that the bromine is in the β-position in the above acid, no matter which value is chosen for the α-place factor. This method for the determination of structure will find much application in the cases where a new substituted paraffin acid is made which has not been previously characterized.

The calculation of the structure from these place factors will be extended to other than the derivatives of the paraffin acids and the α-place factors for different negative radicals will be determined in the near future.

B. Calculation of Ionization Constants from Structure.

In the calculation of structure from the *place factors* as determined above, it is evident that the fairly large errors in the ionization constant will not interfere with the accuracy by which the position of the substituent may be determined. In the determination of the position of the substituent, therefore, the rule of thirds need not hold with an accuracy greater than ten to twenty per cent. for the α, β, γ or δ-positions. In the calculation of ionization constants from structure, however, the rule of thirds must hold with an accuracy equal to that with which the

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ionization constant may be determined, if it is to give accurate results.

The calculation of ionization constants will give a rigid test of this rule. From the knowledge of the value of the α-place factor for a given negative substituent, the ionization constant of any saturated paraffin acid, substituted in any position by this given negative substituent, may be calculated, if we know the ionization constant of the corresponding unsubstituted acid. This will be illustrated by the following example. The ionization constant of β-bromopropionic acid is desired. The α-place factor for bromine, calculated from α bromobutyric acid, is found to be 0.6159. Since the ionization constant of β-bromopropionic acid is desired, applying the rule of thirds, the β-place factor for bromine is $0.6159/3 = 0.2053$. Adding to this value, the factor for the other atoms in the molecule, the result, 1.2053, gives the factor representing the combined influences of all the atoms in the molecule of β-bromopropionic acid. The ratio 1.2053/1 is the ratio between the influences of all the atoms in β-bromopropionic acid as compared to propionic acid. By definition these influences were obtained from

$$1/\log K \text{ (bromopropionic)} : 1/\log K \text{ (propionic)} = 1.2052 : 1.$$

Log K (propionic acid) is known to be —4.83863. Hence $1.2052/1 = -4.83863/X$ where X is the logarithm of the desired ionization constant of β-bromopropionic acid. $X = -4.0154$ or -5.9845, which gives the numerical calculated value for K (β-bromopropionic acid) $= 9.6 \times 10^{-5}$ while the measured value is K (β-bromopropionic acid) $= 9.8 \times 10^{-5}$. In the above calculation, the α-factor for bromine, calculated from α-bromobutyric acid was employed. To show with what accuracy the place factor must be known, the α-place factors for bromine as determined from bromoacetic acid (0.6539) and α-bromopropionic acid (0.6312) when used in the above calculations gives the calculated results 1.04×10^{-4} and 1.00×10^{-4}, respectively. The average for the place factors for α-bromine, as determined from Table I, give the result 1.00×10^{-4}. A difference of four parts in sixty-one in the place factors make a difference of eight parts in ninety-six in the ionization constant. The average value of the α-bromine place factor gives a result about 2 per cent. higher than the experimental value for β-bromopropionic acid, which is in error by that amount. From this single example it appears that the calculated result may fall within the limit of error of the experimental value. The fact that of the seven values necessary for the above calculations six were made by different observers makes the result of more value.

Table II gives the results of other calculations as compared with the experimental values. In the first column under the heading, ionization constant, is given the result using the average of all the α-factors for a given negative substituent given in Table I. The second column, under the same head, gives the experimental values for the same acid and the

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last column, the results calculated from the best value for the α-factor for the given negative substituent.

TABLE II.

Name.	Ionization constants. Calculated from average α-factor.	Measured.	Calculated from single α-factor.
γ-Chlorobutyric acid	$3.5 \; 10^{-5}$	$3. \; 10^{-5}$	$3.4 \; 10^{-5}$
δ-Chlorovalerianic acid	$2.67 \; 10^{-5}$	$2.04 \; 10^{-5}$	$2.66 \; 10^{-5}$
β-Bromopropionic acid	$1.0 \; 10^{-4}$	$9.8 \; 10^{-5}$	$9.7 \; 10^{-5}$
γ-Bromobutyric acid	$3.2 \; 10^{-5}$	$2.6 \; 10^{-5}$	$3.1 \; 10^{-5}$
δ-Bromovalerianic acid	$2.04 \; 10^{-5}$	$1.91 \; 10^{-5}$	$2.03 \; 10^{-5}$
β-Iodopropionic acid	$7.4 \; 10^{-5}$	$9. \; 10^{-5}$	.....
γ-Iodobutyric acid	$2.8 \; 10^{-5}$	$2.3 \; 10^{-5}$	.....
δ-Iodovalerianic acid	$1.95 \; 10^{-5}$	$1.71 \; 10^{-5}$	.....
β-Hydroxypropionic acid	$3.2 \; 10^{-5}$	$3.1 \; 10^{-5}$	$3.2 \; 10^{-5}$
γ-Hydroxybutyric acid	$2.05 \; 10^{-5}$	$1.93 \; 10^{-5}$	$2.03 \; 10^{-5}$
γ-Hydroxyvalerianic acid	$2.1 \; 10^{-5}$	$2.0 \; 10^{-5}$	$2.0 \; 10^{-5}$
β-Phenylpropionic acid	$2.1 \; 10^{-5}$	$2.3 \; 10^{-5}$	$2.2 \; 10^{-5}$
γ-Chlorobutyric acid	$3.0 \; 10^{-5}$	$3. \; 10^{-5}$	$3.0 \; 10^{-5}$
δ-Chlorovalerianic acid	$2.00 \; 10^{-5}$	$2.04 \; 10^{-5}$	$2.00 \; 10^{-5}$

Table II shows that the ionization constants of negative substituted paraffin monocarboxylic acids may be calculated with a fair degree of accuracy from the existing data. It must be borne in mind that the rule of thirds will not hold accurately for acids which do not obey the mass law. It is important to know, therefore, just how accurately the mass law holds for organic electrolytes. In the case of the chloro acids given in Table I a much better agreement between the calculated and experimental values (given in Table II) would be obtained if the value of the experimental β-chlorine factor is taken, rather than that of the α-factor, to calculate the ionization constants of the γ- or δ-chloro acids. The last two acids given in Table II were so calculated. Future experiments will be made to study this point in detail.

Finally, the question, as to whether this additive relation in the free energy of ionization will hold for more than one negative radical in the same molecule or for several different negative radicals, must be settled. For example, the rule of thirds will be applied to glyceric acid, in which there are present an α- and a β-hydroxyl group, as follows:

α-Hydroxyl place factor from α-hydroxypropionic acid = 0.2536
β-Hydroxyl place factor from 0.2536/3 = 0.0843

α- + β-place factors = 0.3378

The factor representing the influence of all the atoms in the molecule of glyceric acid is $1 + 0.3381 = 1.3378$. The corresponding unsubstituted monobasic paraffin acid is propionic acid from which we have:

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$$-4.83863/1.3378 = -3.61633 \text{ or} -4.38367 = 2.4 \times 10^{-5}$$
$$K \text{ (glyceric calculated)} = 2.4 \times 10^{-4}$$
$$K \text{ (glyceric measured)} = 2.0 \times 10^{-4}$$

If we use the α-factor for the hydroxyl groups as determined from glycolic acid (0.2371), the calculated value for the ionization constant of glyceric acid is 2.1×10^{-4}.

Table III will give other examples testing this additive relation. The three columns under the heading ionization constants have the same meaning as under Table II.

TABLE III.

Name.	Substituent and its position.	Ionization constants. Calculated from the average α-factor.	Measured.	Calculated.
Mesotartaric acid	αOH,βOH,βCOOH	5.1×10^{-4}	6.0×10^{-4}	5.8×10^{-4}*
Chlorosuccinic acid	αCl,βCOOH	2.4×10^{-3}	2.8×10^{-3}	2.6×10^{-3}*
Bromosuccinic acid	αBr,βCOOH	2.0×10^{-3}	2.8×10^{-3}?	2.1×10^{-3}*
Phenylsuccinic acid	αC_6H_5,βCOOH	1.54×10^{-4}	1.64×10^{-4}	1.57×10^{-4}*
β-Phenylglutaric acid	βC_6H_5, γCOOH	6.5×10^{-5}	7.7×10^{-5}	6.5×10^{-5}
Tricarballylic acid	βCOOH,βCOOH	2.30×10^{-5}	2.24×10^{-5}	.....
β-Phenyl-γ-acetobutyric acid	(βC_6H_5),[δ(O=)]	3.3×10^{-5}	3.2×10^{-5}	3.2×10^{-5}
Glyoxalic acid	αOH,αOH	5.8×10^{-4}	$5. \times 10^{-4}$	5.20×10^{-4}
Citric acid	αOH,βCOOH,βCOOH	8.0×10^{-4}	8.2 / 8.0 $\times 10^{-4}$	.....

Table III shows that the additive relation of the place factors for different negative groups holds fairly well. It must be remembered that with more than one negative substituent, the factor representing the replaced hydrogen atoms, which is neglected in all the above calculations, may be large enough to influence, slightly, the accuracy of the calculations. The author suspects, however, that the error due to impurities in the reagents used to determin the ionization constants is far greater than that due to neglecting the additive factor for the hydrogen replaced. These calculations, again, show with what accuracy the rule of thirds will hold. In the case of the carboxyl group which does not obey this rule, the additive place factors for the carboxyl groups were calculated from the corresponding unsubstituted dibasic paraffin acids (see Table I, No. 5). This last fact shows that the free energy of ionization (proportional to the logarithm of K) of the paraffin acids is made up additively of the combined direct and indirect influences of each atom or radical in the molecule whether or not the acids obey the rule of thirds. Finally considering tricarballylic and citric acids as derivatives of isobutyric acid rather than of butyric acid, a fine check between the experimental and calculated results is obtained as Table III shows. Hence this additive free energy relationship furnishes us with a means of determining

[1] Using the α-place factor from α-substituted propionic acids.

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which carboxyl group in polybasic acids is ionizing. The experimental study of these place factors is now in progress and will be extended to other classes of compounds.

URBANA, ILL.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WYOMING EXPERIMENT STATION.]

CHEMICAL EXAMINATION OF WOODY ASTER.

BY L. CHAS. RAIFORD.

Received May 15, 1911.

During the past several years thousands[1] of sheep have died in Wyoming through what is supposed to have been the eating of poisonous plants on the ranges. For the last two or three seasons the losses have occurred, in many instances, in localities where the areas grazed were somewhat circumscribed, and in several of these places a certain plant that later came to be suspected as poisonous was found in enormous numbers. It is notable that the heaviest losses for the seasons of both 1908 and 1909 occurred in approximately the same localities, and that in nearly all of these places the suspected plant was abundant.

The facts stated above were secured through a preliminary investigation of the conditions that prevailed, during the seasons mentioned, by both botanist and veterinarian of this station; and, it may be added, the data collected tended to indicate a plant known as the woody aster as the possible source of the trouble. The idea that the losses were due to poisonous plants seemed to be favored indirectly by the inconclusive results of two veterinarians from the Bureau of Animal Industry, who studied the question during the seasons of 1907 and 1908, and who made careful search for animal parasites.[2] Still further support of the view at present entertained was secured from data[3] obtained by the veterinarian of this station during the season of 1910, when extracts prepared in this laboratory from the aster in question were fed to sheep kept under such conditions that the effect of the poison, if any, could be noted. Tests upon other experimental animals are now being conducted with these extracts, and the results so far obtained are in harmony with what has been recorded above.

The suspected plant belongs to the genus *Xylorrhiza*,[4] species of which have been collected in Wyoming, Colorado, and Utah.[5] These plants

[1] Tenth Annual Report of State Board of Sheep Commissioners, 7 (1908).

[2] The losses were at first attributed to the so-called "grub-in-the-head."

[3] *Wyoming Exp. Sta., Bull.* 88.

[4] Pammel, "Manual of Poisonous Plants," p. 138 (1910), designates this plant as the *Aster Parryi Gray*.

[5] According to the statements of herders, stock usually avoid this plant on the range, although analysis shows that it has a relatively high food value.

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appear to be confined to the arid regions, and to soils in which only the so-called alkali-enduring vegetation will thrive. The most abundant species in Wyoming is the *Parryi*, which does not, however, occur over the entire state, but is restricted to certain districts characterized by what is usually known as the adobe or gumbo type of soil, intermixed somewhat with gravel and containing larger or smaller quantities of the salts commonly designated as "alkali." A consideration of further interest in this connection is that this particular plant is not only confined to the type of soil named, but that Wyoming is the center of its distribution. More remarkable[1] yet, perhaps, is the fact that this aster is almost invariably more or less infected with a fungus[2] (*Puccinia Xylorrhiza*); and that in the season of 1910, during which time the sheep losses in Wyoming from suspected poisoning were fewer than in either of the previous years mentioned, this aster was quite free from the fungus. Among the other species of the genus *Xylorrhiza*, of which three or four have been described, only the *villosa*,[3] so far as the writer is aware, has been known[4] to be infected with this fungus; and no other has been suspected of having poisonous properties.[5]

A consideration of the above-mentioned facts seemed to warrant a chemical examination of the suspected plant; and with this in view a considerable quantity of material consisting of both roots and tops[6] was collected during the early part of June, 1910. In grazing, the animal probably gets but a trifle of the root when the top is taken, but it was thought worth while to use both in the preliminary examination.

In the present paper the results of the proximate analyses of both parts of the plant are reported, to which have been added the constituents of the ash in each case. For tests[7] with experimental animals extracts were prepared with different solvents. The results secured seem to indicate that the material extracted by alcohol (from which almost all the alcohol was removed before administration to the animal) had the most pronounced poisonous effect. In a later paper the results of a detailed examination of this extract will be given.

Experimental Part.

Preparation of Material.—As soon as the plant was collected[8] the roots

[1] *Press Bull.* 10, *Wyo. Agr. Exp. Sta.*

[2] This fungus has not been shown to be poisonous, but has been suspected in this connection.

[3] According to some authorities this is a variety of *Parryi*.

[4] Examination made by Dr. A. Nelson, of this Station.

[5] Dr. P. A. Rydberg, New York Botanical Gardens, private communication.

[6] This includes everything above the surface of the ground.

[7] Conducted by the veterinarian of this Station.

[8] This was done while the plant was in bloom.

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were separated from the leaves and tops, and each was spread in a thin layer in the open air and dried thus until all danger of heating up in packages was passed, after which the different parts were placed in separate sacks and sent to the laboratory. When thoroughly air dry all old stems, representing the growth of a previous year, were removed from the leaves and tops, and the remainder was then ground and sieved. The root was cleaned and prepared in the usual way.

Extraction with Different Solvents.—The examination was begun by extracting separate portions of about 2.5 grams each in a Soxhlet apparatus with ligroin (boiling point 25–50°), ether, and alcohol, respectively. The quantities removed are indicated in percentages in Table I.

TABLE I.

	Leaf.		Root.	
	93°[1].	110°.	93°.	110°.
Ligroin (25–50°)	1.66	1.63	0.96	0.90
Ether	2.94	2.86	3.48	3.29
Ether extract, volatil at 110°	...	0.08	...	0.19
Alcohol	28.98	27.90	13.73	13.29

When the solvents ligroin, ether, chloroform, ethyl acetate, and alcohol were used successively on the same samples of drug, the quantities removed were as follows:

TABLE II.

	Leaf.		Root.	
	93°.	110°.	93°.	110°.
Ligroin	1.60	1.59	0.75	0.72
Ether	1.63	1.57	0.88	0.83
Chloroform	1.15	1.14	0.35	0.33
Ethyl acetate	1.88	1.74	0.86	0.82
Alcohol	17.69	16.81	7.61	7.20
Total	23.95	22.85	10.45	9.90

It will be noted that the material removed by alcohol alone (Table I) weighed more than that extracted by all the solvents mentioned in Table II. This difference, which is indicated in Table III, is interpreted to mean that this material became oxidized or otherwise changed during extraction in such a way as to render it partially insoluble; and that the change was facilitated by the increased length of time required for successive extraction with several solvents as against that necessary for treatment with alcohol alone. With the last named liquid the extract began, before extraction was complete, to deposit a solid that could not afterward be dissolved by alcohol. This behavior was noted with both leaf and root, and will be considered later.

[1] Boiling point of water at the altitude of this Station.

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TABLE III.

	Leaf.		Root.	
	93°.	110°.	93°.	110°.
Alcohol	28.98	27.90	13.73	13.29
Solvents of Table II	23.95	22.85	10.45	9.90
Difference	5.03	5.05	3.28	3.39

Proximate Analysis.—The proximate analyses of the plant parts were conducted in accordance with official methods. The results are given in Table IV.

TABLE IV.

	Leaf.		Root.	
	(1)	(2)	(1)	(2)
Moisture[1]	8.27	8.27	6.08	6.02
Ash	10.89	10.98	17.37	17.98
Crude fiber	13.34	13.18	29.40	30.10
Pentosans	12.20	12.25	14.43	14.74
Protein (N × 6.25)	23.00	23.00	8.43	8.62
Dextrin	1.15	1.13	2.32	1.96
Starch by malt	None	None	None	None

Preparation and Analysis of Ash.—Portions of the ground and sieved leaf and root, respectively, were ignited below red heat in a muffle furnace, under which conditions the root gave an ash that was almost white.[2] In case of the leaf the charred material was extracted with hot water and filtered, the residue then burned to a white ash, the filtrate mixed with this ash, and the whole evaporated to dryness on a water bath. The last portions of water were expelled by heating just below redness over a free flame. The resulting solid was at once powdered and preserved in glass stoppered bottles until analyzed.

In general the official methods of the A. O. A. C. were followed in the analyses of these ashes. Certain modifications, however, were necessary. In accordance with the official method it is expected that the filtrate[3] obtained when sand, soluble silica and carbon are removed will contain all iron present and other ash components soluble in hydrochloric acid. As a matter of fact, with the ashes here involved, a very considerable quantity of iron (and probably other substances) did not go into solution under the conditions prescribed, and was invariably found in that portion of the material in which soluble silica was determined. In order to account for this, the filtrate obtained during the soluble silica determination was mixed with the first one (Solution A), and the resulting

[1] Determined by heating to constant weight in a stream of hydrogen at the boiling point of water.

[2] Though this ash did not fuse when heated at the higher temperature required by the official method for residues from which soluble matter had been extracted at this stage, a control showed that considerable material was volatilized.

[3] Designated by the official method as Solution A.

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liquid used for the estimation of iron, aluminum, phosphorus pentoxide, etc. But it was thought worth while, before the last named determinations were made, to evaporate the combined filtrates to dryness and remove the remaining silica. This[1] was done in the usual way, and the results obtained, in addition to those secured in accordance with the official method, are given in Table V. Duplicate determinations are reported on the ashes of both leaf and root.

TABLE V.—SOLUBLE SILICA.

		Official method.	Second evaporation.	Total.
Leaf	1	3.43	1.24	4.67
	2	4.09	0.53	4.62
Root	1	12.30	1.42	13.72
	2	12.67	1.03	13.70
Root[2]	1	13.69	0.51	14.20
	2	13.23	1.07	14.30

Average = 0.96 per cent.

It will be seen from these results that the duplicate determinations did not agree in any series when the work was done in strict accordance with the official method, but that close agreement was secured in all

TABLE VI.—CONSTITUENTS OF ASH.

	Leaf.			
	(1)	(2)	(3)	(4)
Moisture	0.67	...		
Chlorine	10.91	10.89		
Carbon dioxide	14.16	14.23		
Sand	2.39	2.56		
Carbon	0.31	0.29		
Soluble silica	4.67	4.62		
Sulfur trioxide[3]	4.89	4.91	10.51[4]	11.08
Phosphorus pentoxide	5.31	5.10		
Ferric oxide	1.42	1.62		
Aluminum oxide	1.70	1.30		
Manganese	trace	trace		
Calcium oxide	12.10	12.42		
Magnesium oxide	4.90	4.95		
Sodium oxide	20.92	20.71		
Potassium oxide	17.41	17.19		

[1] Not required by the official method.

[2] The second series of results from root ash were obtained from material that had not been specially prepared for these analyses, and no other determinations were made on it. Silica estimations were made for the sole purpose of confirming conclusions already reached.

[3] This was determined after iron and aluminum had been removed. See *Z. anal. Chem.*, 19, 419; *J. prakt. Chem.*, 39, 321; and THIS JOURNAL, 24, 658 (1902).

[4] These figures represent total sulfur determined by the peroxide method, and calculated as sulfate in terms of the ash.

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cases when the method was modified to include the silica removed by a second evaporation. The average additional amount obtained thus was 0.96 per cent. The difference in the total amount of iron that resulted through mixing the filtrate from the determination of soluble silica with Solution A was not estimated, but the color of this filtrate indicated that the additional amount of iron was probably as great as in the case of silica.

The composition of the leaf ash is given in Table VI.

TABLE VII.—CONSTITUENTS OF ASH.

	Root.			
	(1)	(2)	(3)	(4)
Moisture	1.25	1.23		
Chlorine	0.79	0.91		
Carbon dioxide	6.42	6.59		
Sand	39.63	39.17		
Carbon	0.84	0.91		
Soluble silica	13.72	13.70		
Sulfur trioxide	1.37	1.45	2.93	2.81[1]
Phosphorus pentoxide	1.52	1.43		
Ferric oxide	...	2.56		
Aluminum oxide	...	5.53		
Manganese	trace	trace		
Calcium oxide	19.32	19.22		
Magnesium oxide	2.80	2.60		
Sodium oxide	2.62	2.35		
Potassium oxide	4.28	4.31		

The composition of the root ash is given in Table VII.

A consideration of the figures representing the various analyses of the woody aster shows that the results of duplicate determinations do not agree very well, and that this disagreement is more marked in the case of the root. These differences are apparently due to the difficulty in securing a uniform sample, a condition which probably depends, so far as the root is concerned, upon the relatively high percentage of sand present in the prepared material. The large amount of substance removed in the analysis of the root at the point where, in accordance with the official method, sand should be obtained led at first to the suspicion that a portion of this substance might be barium sulfate. This suspicion was based largely on the fact that only a small percentage of sulfate was found in the combined filtrate (Solution A) left after determining sand, soluble silica, etc.; and upon the probable presence of considerable quantities of sulfates in the soil[2] where the plant grew. In order to determine

[1] Represents total sulfur determined by peroxide method.

[2] The soil from which this particular sample of aster was collected has not been examined by the writer, but the presence of relatively large amounts of "alkali" (consisting largely of the chloride and sulfate of sodium) in all the soils in that vicinity leaves little doubt of the presence of sulfates in the "aster patches."

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the presence or absence of barium sulfate, a portion of the original root ash was fused with a mixture of sodium and potassium carbonates, and total silica determined in the usual way. After being ignited and weighed, the resulting mass was heated with hydrofluoric and sulfuric acids until constant in weight.[1] The amount of sand and soluble silica determined by the modification of the official method already described was 52.87 per cent., while determination of total silica by fusion gave 49.87 per cent. Now, the presence of iron in the filtrate (containing soluble silica) from sand, previously noted, made it seem almost certain that the latter, also, contained iron. This view was confirmed by showing that the filtrate from total silica by fusion contained a larger amount of iron than did Solution A. The percentage of ferric oxide in the ash, as determined in Solution A, was 2.56 per cent.; that in the filtrate from total silica was 2.88 per cent. Undoubtedly a redetermination of other bases would have shown sufficient increases to account for the difference between the sum of sand and soluble silica in one analysis, and total silica in the other.

An assay of the leaf having shown that alkaloids were absent, attention was next directed to the alcoholic extract. It is worthy of note that in the preliminary consideration of this extract some of the matter (of which a large part seemed to be resin) removed was changed by oxidation or otherwise so rapidly that before the drug was exhausted the extract began to deposit a solid that could not afterward be dissolved in alcohol. In future work the amount separating at this stage will be determined as nearly quantitatively as possible, and other properties will be examined. This behavior, taken in connection with the statement already given regarding the poisonous character of the extracts prepared with various solvents, makes necessary a detailed study of the alcoholic extract. The work is now in progress.

LARAMIE, WYOMING,
May, 1911.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 193.]

STUDIES ON AMYLASES: III. EXPERIMENTS UPON THE PREPARATION AND PROPERTIES OF PANCREATIC AMYLASE.[2]

BY H. C SHERMAN AND M. D. SCHLESINGER.

Investigations in this laboratory during the three years, 1907–1910, resulted in the development of a method for the determination of amylolytic power[3] and a somewhat extended quantitative study, by means of this method, of the action of pancreatic amylase.[4] On the basis of

[1] The slight non-volatile residue left contained iron, but spectroscopic examination failed to show even a trace of barium.

[2] Read before the New York Section, American Chemical Society, May, 1911.

[3] Sherman, Kendall and Clark, THIS JOURNAL, 32, 1073.

[4] Kendall and Sherman, *Ibid.*, 32, 1087.

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this work we have been able to make use of activity as a criterion in extending our investigation to the preparation and study of a pancreatic amylase of much higher concentration and purity than had previously been available.

Of the numerous studies of amylases recorded in the literature the greater number deal only with extracts or secretions and when solid preparations have been described the amylolytic activity has not always been determined quantitatively.

Only a few previous investigations are therefore directly comparable with the experiments to be described in this paper, and these deal mainly with vegetable amylases.

Lintner[1] used a method which consisted essentially in extracting the enzyme from malt by means of water or very dilute alcohol, precipitating by strong alcohol, and purifying by repeated solution and reprecipitation. Of several preparations thus obtained the strongest had such diastatic power that 0.12 mg. acting upon 10 cc. of 2 per cent. soluble starch for one hour at room temperature formed enough sugar to reduce 5 cc. of Fehling's solution. One preparation of this strength was obtained from barley malt and one from wheat malt. Lintner proposed that these preparations be considered as having a strength of 100, and that the amylolytic powers of other precipitated diastases be expressed upon this scale. In one of his most active preparations Lintner found: Carbon, 44.33 per cent.; hydrogen, 6.98 per cent.; nitrogen, 8.92 per cent.; sulfur, 1.07 per cent.; oxygen, 32.91 per cent.; ash, 4.79 per cent. Lintner's diastases are described as giving the typical reactions of proteins.

Osborne[2] by a process of successive precipitation with ammonium sulfate and dialysis followed by a fractional precipitation by dialyzing against alcohol, obtained from an extract of barley malt a preparation having a diastatic power of 600 on Lintner's scale. This preparation showed 0.66 per cent. ash and the following composition calculated to the dry ash-free basis: Carbon, 52.50 per cent.; hydrogen, 6.72 per cent.; nitrogen, 16.10 per cent.; sulfur, 1.90 per cent.;[3] oxygen, 22.78 per cent. This substance gave "all the usual protein reactions" and yielded a flocculent coagulum when heated in solution. Osborne advanced the hypothesis that active diastase is a combination of albumin with some other substance, presumably a proteose, which combination breaks up on heating, yielding a coagulated albumin.

Other investigators, among whom may be mentioned Zulkowski,[4]

[1] *J. prakt. Chem.*, [2] 34, 378 (1886); 36, 481 (1887).

[2] THIS JOURNAL, 17, 593, 598, 601–3 (1895).

[3] Osborne suggests that the high figure for sulfur in this preparation may be due to the retention of a little of the sulfate employed in the process of its purification.

[4] *Wien Akad.*, 71, II, 453; 77, II, 647; *Jahr.-Thierchem.*, 5, 268; 8, 356.

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Loew,[1] Szilagyi,[2] Jegorow,[3] Egroff,[4] Wroblewski,[5] Sykes and Hussey,[6] Frankel and Hamburg,[7] have also described preparations of malt or wheat diastase but without evidence of having secured any higher concentration of amylase than existed in Osborne's preparation.

Hüfner,[8] described in some detail an amylolytic preparation from the pancreas, but gave no quantitative data as to its activity.

Vernon[9] extracted pancreas glands with glycerol and precipitated with alcohol. Although many preparations were made under varying conditions the greater part of the diastatic power was always lost. Vernon concluded that the addition of alcohol to glycerol extracts of pancreas results in rapid destruction of its amylase.

Experimental.

Having in the course of previous work[10] been much hampered by deterioration of amylolytic power in pancreatin solutions, we preceded our attempts to purify pancreatic amylase by a number of experiments to test the influence of different solvents and precipitants upon the amylolytic activity of commercial pancreatin, the material which has served as a starting point for most of our preparations. The pancreatin showed marked loss of amylolytic power on standing 24–48 hours in water, brine, 5 per cent. salt solution, or in water containing the small amounts of salt and phosphate which had been found necessary to enable the enzyme to show its full activity.[10] For this reason the method used by Osborne in purifying malt diastase did not seem well adapted to pancreatic amylase.

Vernon's observation that extraction with glycerol followed by precipitation with alcohol involved a large destruction of amylase, or at least a large loss of amylolytic power, was also confirmed in our preliminary experiments.

On the other hand it was found that pancreatic amylase was fairly permanent in 50 per cent. alcohol and could be recovered in active form from this solvent by precipitation with strong alcohol or with a mixture of alcohol and ether. Using 7 volumes of a mixture of 20 per cent. alcohol and 80 per cent. ether, the precipitate was obtained as a yellowish, oily product, very readily soluble in water. This precipitate on account of its mechanical condition could not readily be transferred, but after the

[1] *Pflüger's Archiv. f. d. ges. Physiol.*, **27**, 203.
[2] *Chem.-Ztg.*, 1891, 349.
[3] *Jour. russ. chem. Ges.*, **25**, 80; *Chem. Centralbl.*, 1893, II, 212.
[4] *Mon. Sci.*, [4] **8**, II, 741.
[5] *Ber.*, **30**, 2289; **31**, 1127.
[6] *Jour. Fed. Inst. Brew.*, **4**, 527; *J. Chem. Soc.*, **76**, I, 313 (1899).
[7] *Hofmeister's Beitrage*, **8**, 389.
[8] *J. prakt. Chem.*, [2] **5**, 372 (1872).
[9] *Jour. Physiol.*, **29**, 302 (1903).
[10] Sherman, Kendall and Clark, *Loc. cit.*

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removal of the supernatant liquid was dissolved in water and poured into about 3 volumes of absolute alcohol, thus bringing it into the form of a flocculent precipitate which could be filtered, washed with ether, and dried over sulfuric acid.

Preparation 1, made as just described from a commercial pancreatin having a diastatic power of 101 (Lintner's scale), showed a diastatic power of 402 on the same scale.

Preparations 2 and 3 made in approximately the same way from the same material showed diastatic powers of 306 and 450 (Lintner scale) respectively.

Preparation 4.—About 0.5 gram of preparation 2 was mixed with about 30 cc. of 65 per cent. alcohol in which it did not entirely dissolve, transferred without filtering to a small collodion sack, and dialyzed for 6 hours against 200 cc. of 65 per cent. alcohol. The dialyzate showed no diastatic power. The liquid in the sack was then filtered, the filtrate poured into absolute (Kahlbaum's 99.8 per cent.) alcohol, ether added, and the precipitate filtered out, washed with alcohol and ether, and dried over sulfuric acid. This preparation showed a power of 531 (Lintner scale) and was therefore over 5 times as strong as the pancreatin from which it was prepared, and about 88 per cent. as strong as Osborne's strongest malt diastase.

In the next preparation the precipitation and dialysis were carried out somewhat differently.

Preparation 5.—Ten grams of commercial pancreatin were thoroughly stirred with 250 cc. of 50 per cent. alcohol, filtered, and 200 cc. of the filtrate poured into a mixture of 1120 cc. ether and 280 cc. alcohol. A yellow, oily precipitate was obtained. The supernatant liquid was decanted through a filter and the precipitate (still wet with alcohol and ether) was dissolved in as little water as possible, filtered, and poured into about 5 volumes of absolute alcohol. A white flocculent precipitate separated at once. A small amount of ether was then added as this seems to facilitate the subsequent handling of the precipitate. The precipitate was then separated by filtration, dissolved in as little 50 per cent. alcohol as possible, and dialyzed in a collodion sack for three days against 50 per cent. alcohol, which was renewed twice daily. The successive dialyzates showed biuret reaction but with constantly decreasing intensity indicating that this treatment was efficient in removing certain of the protein impurities from the enzyme solution. At the same time a precipitate separated from the enzyme solution within the sack. This precipitate, when removed by filtration and thoroughly washed with 50 per cent. alcohol, was found not to have diastatic power. It was insoluble in water, but soluble in salt solution.

The solution containing the enzyme, after having been thus dialyzed and filtered, was mixed with a large volume of ether and a small volume of absolute alcohol. A white flocculent precipitate formed readily and settled in about half an hour. The liquid was then decanted and the precipitate washed by decantation with alcohol-ether mixtures, the proportion of alcohol being decreased and of ether increased until the water was removed, then washed with absolute ether and dried over sulfuric acid. This preparation weighed 0.09 gram and showed a diastatic power of 790 on the new scale, corresponding to 1168 on Lintner's scale.

Preparations 6–15.—Here the method used for preparation 5 was modified in different ways, as by dialyzing for various lengths of time, and by the use of amyl alcohol or acetone as precipitant. All of these preparations were inferior to preparation 5 in diastatic power.

Preparation 16.—A sample of commercial pancreatin having a diastatic power of 150 (new scale)[1] was extracted with 50 per cent. alcohol, filtered, the filtrate pre-

[1] Sherman, Kendall and Clark, THIS JOURNAL, 32, 1082–4.

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cipitated with alcohol-ether mixture, the precipitate thus obtained dissolved in water, reprecipitated by strong alcohol, and redissolved in 50 per cent. alcohol as in preparation 5. To this solution, which measured about 150 cc., we added 8 grams of maltose dissolved in a little water, thinking that this maltose might protect the amylase from deterioration, as Hudson has found it possible to protect invertase by sucrose under somewhat analogous circumstances. This solution was then dialyzed against 50 per cent. alcohol as in preparation 5. At the end of 19 hours the outer solution was replaced by fresh 50 per cent. alcohol; dialysis against the second portion of alcohol was continued 5 hours against the third 18 hours and against the fourth 49 hours —a total of 91 hours' dialysis. The solution in the collodion sack was then filtered, the filtrate shaken with 3–4 volumes of a mixture of equal parts of absolute alcohol and ether, the precipitate thus obtained dissolved in a small amount of water, reprecipitated by pouring into alcohol, filtered in dry air, and dried in partial vacuum over sulfuric acid.

This preparation showed a diastatic power of 1528 on the new scale[1] corresponding to 2270 on Lintner's scale.

A very dilute solution of this preparation in pure water yielded a white flocculent coagulum on heating. The solution was boiled down to about 10 cc. and filtered. The coagulum was submitted to the biuret test at the same time and in exactly the same manner as the filtrate. The filtrate gave the rose reaction characteristic of proteose or peptone, while the coagulum gave a blue-violet reaction such as is commonly observed with albumins. This result is in accordance with Osborne's suggestion, based on his study of malt diastase, that the enzyme may be a compound of a coagulable albumin with a proteose.

Preparation 17.—This was prepared in practically the same manner as the preceding, except that 10 grams of maltose (instead of 8 grams) were added to protect the enzyme from deterioration, and the time of dialysis was shortened, *viz.*, 17 hours for the first period, 23 hours for the second, and 28 hours for the third—a total of 68 hours. Although the dialysis in this case was not carried to completion, the last dialyzate containing maltose and giving a distinct biuret reaction, the product showed a diastatic power of 1910 on the new scale, corresponding to 2760 on Lintner's scale.

This preparation gave the same coagulation and biuret tests as preparation 16. This has also been found true of all subsequent preparations so far as tested, and will therefore not be repeated in the descriptions which follow.

Preparations 18 and 19, in which the method was varied, yielded products of lower diastatic power than the preceding.

Preparation 20.—Twenty grams of pancreatin 4,[2] carried through the same process as preparation 17, gave a product whose activity was 2000 on the new scale, corresponding to a Lintner figure of 2950.

Preparations 21–23 representing other experimental variations in the method showed no advance in diastatic power.

Preparation 24.—In this case parchment paper thimbles instead of collodion sacks were used for dialyzing. The final product appeared more powdery than in other

[1] Up to this point tests of diastatic power had been made by dissolving the enzyme in pure water and measuring portions of this solution into starch solutions containing the activating agents. This and the following preparations were dissolved at once in water containing the activating agents in order to avoid the deterioration which takes place in pure water.

[2] This sample of pancreatin which was used in preparations 19–28 was from the same source as that previously used, but showed an activity of 158 (new scale) corresponding to 228 on Lintner's scale.

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cases, and showed a power of 2280 new scale, equivalent to a Lintner figure of 3360, but from the slowness with which the dialyzate acquired the yellow color of the enzyme solution, and from the results of tests for proteins in the dialyzate, it was judged that the removal of impurities went on less readily through the parchment than through the collodion membrane, and the latter was therefore used for subsequent preparations.

Preparation 25.—In this case the maltose for protection of the enzyme was added after 16 hours' dialysis and the removal of the first dialyzate. The dialysis was continued 64 hours in all, with three changes of dialyzate. The filtered solution was then mixed with an equal volume of a mixture of equal parts of alcohol and ether, the resulting precipitate dissolved in water, and reprecipitated by dropping into two volumes of absolute alcohol. The final product showed an activity of 2092 on the new scale, corresponding to 3090 on Lintner's scale.

Preparation 26 was made in practically the same manner as preparation 17, except that 5 grams of maltose (instead of 10 grams) were used to protect the enzyme during dialysis. This product showed an activity of 2280 (new scale) corresponding to a Lintner figure of 3360.

Preparations 27–30 showed no advance in diastatic power.

Preparation 31.—The starting material for this preparation and for all which follow, except preparation 37, was a new sample of commercial pancreatin (pancreatin 5) from the same source as the pancreatins previously used, but presumably made by an improved process since it showed an activity of 425 on the new scale of diastatic power.

Twenty grams of pancreatin 5 were submitted to practically the same process as in preparation 26, up to the point of beginning of dialysis. Here the work was interrupted and the solution of enzyme and maltose in 50 per cent. alcohol stood over night in a beaker. It was then placed in a collodion sack and dialyzed 29 hours against 2 liters of 50 per cent. alcohol, which was kept in circulation during the working hours of the day. The final product after washing with ether and standing over sulfuric acid in partial vacuum until air-dry weighed 0.7 gram and showed a power of 3120 (new scale) corresponding to a Lintner figure for the same temperature of 4520.

Preparation 32.—This was a duplication of preparation 31 except that the solution as soon as prepared for dialysis was placed in a collodion sack and dialyzed against 300 cc. of 50 per cent. alcohol at rest over night, then for 7 hours against a fresh portion of 2 liters kept in circulation, then for 16 hours against another portion of 2 liters at rest. The last dialyzate showed only a very slight biuret reaction. Total time of dialysis 40 hours; weight of air-dry product 0.65 gram, or 3.25 per cent. of the weight of original material; activity 3480 (new scale) corresponding to a Lintner figure for the same temperature (40°) of 5140.

Preparation 33.—This was prepared in the same manner as the preceding, except in dialysis. It was dialyzed about 40 hours in all against 4 portions of 50 per cent. alcohol, each 1200 cc. The last dialyzate was not entirely free from maltose and also showed a slight biuret reaction. The activity of the air-dry product was 3360 (new scale).

Preparation 34.—In this preparation the volume of each dialyzate was 2000 cc. instead of 1200 cc., otherwise it was prepared in the same manner as No. 33. Yield, 0.51 gram; activity, 3430 (new scale).

Preparation 35.—Prepared in the same manner as No. 34. Yield, 0.93 gram; activity, 3450 (new scale).

Preparation 36.—Prepared like Nos. 34 and 35, except in dialysis, which was continued only 19 hours, though with 5 changes of dialyzate. This was evidently insufficient to remove all of the added maltose, as the last dialyzate showed maltose

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and the final product had a greater weight (1.08 gram) and a lower activity (2880) than the preceding preparations. Further evidence that this preparation was contaminated with maltose is found in the fact that the nitrogen content of the dry ash-free substance was only 13.65 per cent., while that of preparation 35 was 15.58 per cent.

Preparation 37.—Twenty grams of a commercial pancreas powder (H) from a different manufacturer than those previously used and which showed an amylolytic power of 405 (new scale) was subjected to the same process as in preparations 34 and 35 and yielded 0.87 gram of air-dry product, the activity of which was 3260 (new scale).

On the Probable Purity of these Preparations.

At present the principal criterion of purity or concentration of any enzyme preparation is its activity. Judged from this standpoint, it would seem that our later preparations must represent a high concentration of pancreatic amylase, since they exhibit about 8 times the amylolytic power of the strongest preparations which we have found described in the literature or which we have been able to obtain commercially. On the other hand, the nature of our products and the method of their preparation preclude the belief that they are chemically pure. Like other preparations of a protein nature they contain moisture and ash even after having been through an extended course of purification. It is possible that our preparations may contain traces of maltose, since the maltose used to protect the enzyme from deterioration is not always completely removed by dialysis and the minute amount sometimes remaining in the enzyme solution might not be completely excluded in the final precipitation. The presence of any considerable proportion of maltose or of other carbohydrate matter is, however, practically precluded by the analytical data given beyond, which show that our strongest preparations have essentially the composition and character of proteins. To what extent we have succeeded in separating amylase from other materials of a protein nature is a much more difficult question. In the extraction with 50 per cent. alcohol, which constitutes the first step in our process, much of the protein matter is left behind. The second step which consists in precipitating with a limited amount of alcohol and ether, evidently effects a further separation of the enzyme either from protein or other impurity, since the use of a larger amount of the alcohol-ether mixture yielded a heavier precipitate of lower diastatic power. When the solution of enzyme is dialyzed in 50 per cent. alcohol, material which responds to the biuret reaction passes into the dialyzate, and at the same time there occurs a gradual deposition within the collodion sack of protein matter[1] which is then removed by filtration before the final precipitation of the enzyme. Under these conditions, it would seem reasonable to expect a fair approach toward a separation of the

[1] This material is probably a globulin, soluble in 50 per cent. alcohol in the presence of salts, but insoluble when the salts are removed by dialysis. As noted above, it is insoluble in water but soluble in salt solutions.

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enzyme from the unrelated proteins which accompany it in the pancreas. Whether those proteins which are closely related to the amylase are separated by the same process is still doubtful. If the amylase is formed from pre-existent protein, the difference between the enzyme and its precursor may or may not be sufficient to permit their separation by the process here used. Similarly, when a preparation deteriorates as this amylase does, for example, in water solution, there is doubtless some chemical change in the enzyme, but whether this is of such a nature as to permit the separation of the active and inactive forms by any process of dialysis and precipitation it is at present impossible to say. With the single exception of preparation 36, which was dialyzed only 19 hours, and evidently was not free from maltose, all of our later preparations show considerable similarity in amylolytic activity as is apparent from the following summary:

Preparation. No.	Activity-new scale.	
	Substance as tested.	Calculated to dry substance.
31	3120	3310
32	3480	3670
33	3360	3540
34	3430	3570
35	3450	3720
37	3260	3320
Mean of these six preparations.....		3520
Extreme deviations from the mean —6.0 to +5.7 per cent.		

In view of the well-established fact that as enzymes are freed from the substances which ordinarily accompany them in nature, they become much more sensitive to external conditions and the quantitative measurement of their activity, always a sufficiently difficult problem, becomes much more difficult, these figures are significant for their agreement. That six independent preparations of this character should show such close agreement in diastatic power is a strong indication that this method of purification yields a fairly definit result.

Properties.

Some further properties of the preparations just described may be briefly summarized. The amount of material did not permit a detailed examination of each separate preparation, nor is this called for in view of the similarity of the six strong preparations. Each of the following statements of properties represents results obtained upon one or more of these six preparations.

The amylase as here prepared is obtained, depending upon the way in which the final precipitate is handled in washing and drying, either as a friable white powder, or as brittle, easily pulverized, slightly yellowish scales resembling dry egg albumin. It dissolves readily in water to a clear colorless solution.

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It gives pronounced xanthoproteic and tryptophane reactions and also gives a typical protein reaction in the biuret test and with Millon's reagent.

Its water solution coagulates on heating, exhibiting the same appearance in this respect as an ordinary albumin. The coagulum gives a blue-violet reaction, while the filtrate gives a rose-pink reaction, to the biuret test. This filtrate if dropped into alcohol gives a white, flocculent precipitate.

In an experiment upon the temperature of coagulation a water solution containing 1 mg. per cubic centimeter showed opalescence at 60–65°, distinct turbidity at 70–75°, and a flocculent precipitate at 80°. Held at 80° until the precipitate had gathered into a few large flocks and then heated to boiling, no further precipitation occurred.

The air-dry preparations contained from 1.8–7.4 per cent. of moisture, and from 2.2–2.6 per cent. of ash. Ultimate analyses calculated to dry ash-free material showed:

Preparation. No.	Carbon. Per cent.	Hydrogen. Per cent.	Nitrogen. Per cent.	Oxygen and sulphur. Per cent.
31	52.8	6.7	15.5	25.0
35	53.1	6.6	15.6	24.7

These analyses, taken in connection with the properties already described, sufficiently demonstrate the protein nature of these preparations. Lack of material prevented more detailed study of the ultimate composition.

Regarding the activity of these preparations, the figures given above, 3120–3450 on the new scale of diastatic power, correspond to Lintner's figures of about 5000 for the same temperature (40°). Osborne gives the activity of his strongest malt diastase as 600 on Lintner's scale. It is difficult to decide whether it necessarily follows that our preparation of pancreatic amylase is actually 8 times as active as Osborne's amylase of malt, because of differences in experimental methods.

Wohlgemuth, in his work on saliva and other physiological fluids and tissues, has introduced a method of expressing diastatic power in terms of the number of parts of 1 per cent. solution of Kahlbaum soluble starch which are digested to products giving no reaction with iodine by one part of the substance under examination, usually during 30 minutes at 38°. Thus determined and expressed, the activity of our preparation 34 is:

$$D_{30}^{38} = 500{,}000.$$

The same preparation acting on 2 per cent. soluble starch formed 6,000 times its weight of maltose in 20 minutes at 40°. In 3 hours at the same temperature it digested 100,000 times its weight of starch, and produced 41,500 times its weight of maltose, together with dextrins which gave with iodine a purplish wine color. In 4 hours these dextrins had

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been digested beyond the "erythrodextrin stage" and in 5 hours the 100,000 parts of starch had been completely digested to products giving no color reaction with iodine, and the enzyme had formed 55,500 times its weight of maltose. In 6 hours this preparation digested 200,000 times its weight of starch to the "erythrodextrin stage" with the production of 91,800 times its weight of maltose.[1] Mixed with 400,000 times its weight of starch it digested this in 10 hours to a stage which no longer gave with iodine the starch-iodide blue but instead a rich plum color. At this stage it had formed 118,000 times its weight of maltose. Within 22 hours it had digested the 400,000 parts of starch to the "erythrodextrin stage" and had formed 182,000 times its weight of maltose. In 30 hours it formed 211,000 times its weight of maltose. At the end of 48 hours the starch had been completely digested into products giving no color reaction with iodine.

We take pleasure in acknowledging our indebtedness to the Parke, Davis Company and to Messrs. Fairchild Brothers and Foster for the materials used in the later part of our work and from which we obtained our strongest preparations.

Summary.

By means of a process involving extraction of the dry pancreas powder with 50 per cent. alcohol, repeated precipitation, and purification by dialysis in 50 per cent. alcohol, preparations having diastatic powers up to 3480 on the new scale, corresponding to over 5000 on the Lintner scale or to D^{38}_{30} = 500,000 on Wohlgemuth's scale were obtained.

Six independent preparations showed in the dry substance activities of 3310, 3670, 3540, 3570, 3720, 3320. This agreement indicates that these preparations are substantially alike and that the process yields a fairly definit result.

This product shows the composition and characteristic reactions of a protein closely resembling Osborne's malt diastase, but differs from malt diastase as described by Osborne in its greater activity and in the conditions governing its action.

The pancreatic amylase as here prepared acting at 40° on soluble starch made by the Lintner method formed 6000 times its weight of maltose in 20 minutes and 211,000 times its weight in 30 hours. It digested 400,000 times its weight of starch to the "erythrodextrin stage" in less than 22 hours, and to products giving no reaction with iodine in 48 hours.

LABORATORY OF FOOD CHEMISTRY.

[1] Between 10 and 22 hours this solution ceased to give any reaction with iodine whatever.

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[FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY OF WASHINGTON UNIVERSITY MEDICAL SCHOOL.]

"SUGAR SAND" FROM MAPLE SAP; A SOURCE OF MALIC ACID.

BY W. H. WARREN.

Received May 1, 1911.

When the sap of the sugar-maple tree (*Acer saccharum*) is evaporated, there always appears a variable quantity of a sandy, insoluble substance called "sugar sand" and "niter," the main constituent of which is a calcium salt of malic acid. Some of this material is deposited on the pan, as the sap approaches the sirup-stage, but more of it is in suspension in the sirup from which it is removed by straining. A considerable quantity of *sugar sand* may be collected in this way. Apparently the only analysis of this material thus far published is that which appeared in the "Indiana Station Report for 1899." As this analysis shows a calcium malate content of only 33 per cent., and was clearly made with material which cannot be regarded as typical, it has seemed worth while to make a further examination of this substance.

Collection of Sugar Sand.

This material is not deposited until the sap approaches the sirup-stage when the temperature is 102–103°. It is advisable to reject the deposit on the pan and take only what is suspended in the sirup. As the sirup cools, the *sugar sand* settles to the bottom of the container. The sirup should be drawn from the sediment which should then be mixed with water to dilute adhering sirup and poured upon a flannel strainer. It should be washed until free from sugar and then spread out in a moderately warm place to dry. When reasonable care is taken to collect as much as possible, from 16–25 pounds may be obtained from about one thousand maple trees in the course of the sugar season. The material used for analysis came from Vermont.

Properties and Analysis of Sugar Sand.

General Properties.—When practically free from sugar, this material forms a coarse powder which appears crystalline under the microscope. It has a light gray color, is tasteless and has a slight odor. It is slightly soluble in water, for repeated treatment with this solvent always gives a filtrate containing calcium. Some samples treated with water give solutions having an acid reaction, whereas other samples give neutral solutions. I have never had a sample which gave an alkaline reaction. Treated with dilute hydrochloric acid, *sugar sand* passes into solution except most of the silica and a small amount of organic matter of unknown composition.

Moisture.—Dried at 110° to constant weight *sugar sand* loses 2.6 per cent. of water.

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Loss on Ignition and Ash.—Two determinations of ash after ignition in the blast-lamp flame to constant weight gave a loss of 67.74 per cent. and 32.26 per cent. of ash; and a loss of 67.81 per cent. and 32.19 per cent. of ash.

Analysis of Ash.—A qualitative examination of ash showed that it consisted mainly of calcium with small quantities of magnesium and iron. The only acids were silica and a very small quantity of phosphoric acid. Two quantitative analyses were made of the ash obtained in the preceding ash determinations. The usual analytical methods required for the quantitative separation of the bases and acids mentioned were used and gave the following results:

	1.	2.
Calcium (CaO)	24.03	23.87
Iron (Fe_2O_3)	0.39	0.46
Magnesium (MgO)	0.05	0.07
Silica (SiO_2)	7.74	7.76
Phosphoric acid (P_2O_5)	0.05	0.09
	32.26	32.25
Percentage of ash	32.26	32.19

Organic Acids.—The value of *sugar sand* is wholly dependent upon its malic acid content, the only organic acid present in any quantity. In using this material to prepare pure malic acid and its salts, it is necessary to have some means of determining the exact amount of this acid in the crude product. For this purpose, I have used the following simple method of analysis which is fairly rapid and gives closely agreeing results.

Heat about a gram of material on the water bath for an hour with 25 cc. of normal oxalic acid. Filter into a 250 cc. graduated flask, first decanting the clear supernatant solution upon the filter, then adding the precipitate and washing the latter thoroughly with hot water. Cool the filtrate and bring its volume to 250 cc. with distilled water. The final solution is nearly colorless.

Measure from a buret, or pipet, two separate 50 cc. portions of this solution. Determine in one portion the total acidity by titration with decinormal sodium hydroxide solution. This gives not only the acidity caused by the organic acids in the material, but also that due to the excess of oxalic acid used to decompose the calcium salts. To determin the excess of oxalic acid, acidify the second portion of solution with acetic acid and precipitate calcium oxalate by means of calcium chloride. Collect the precipitated calcium oxalate upon a filter, ignite and weigh as calcium oxide. Since 0.0028 gram of calcium oxide are equivalent to 1 cc. of decinormal sodium hydroxide solution, the quantity of decinormal alkali required to neutralize the organic acids in *sugar sand* can be deter-

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mined. Three determinations of organic acids (calculated as malic acid) in the same sample showed that it contained 52.33, 52.25, and 52.19 per cent.

Therefore, calculated as malic acid, the average percentage of organic acid in *sugar sand* by this method of analysis is 52.26. It would be natural to expect material of such origin to contain more than one organic acid. But, although many experiments have been made for the purpose of isolating other organic acids, I have succeeded thus far in finding only a mere trace of oxalic acid. This latter acid was recognized by the characteristic envelope-shaped crystals of calcium oxalate seen under the microscope. The amount, however, was so small and the quantity of *sugar sand* used in the experiment so large that I think not much importance should be attached to the result.

Sugar.—The fact that *sugar sand* is precipitated from a concentrated sugar solution would lead one to expect the presence of sugar in this material. The quantity of free sugars, however, can be greatly reduced by thorough washing, but sugar combined with lime might not be removed so easily. The "Indiana Station Report for 1899" records an analysis of "niter" or "sugar sand" which gave 12.74 per cent. of reducing sugars and 26.88 per cent. of non-reducing sugars (cane sugar). Unless these sugars were combined with calcium oxide, which could hardly have been the case, their presence in such quantities could have been detected by tasting. Sy[1] remarks concerning this analysis that it was evidently a "niter" which contained considerable sugar or sirup. Such undoubtedly was the case and for that reason an analysis of typical *sugar sand* was not made in that instance.

The presence of sugar in the material I have examined cannot be detected by tasting, as it is tasteless. Yet a small quantity of sugar might be present without being detected in this way. Commenting further upon the Indiana analysis, Sy says that part of the sucrose is probably present as calcium sucrate. Therefore, in examining this material for sugar, I had three things in mind, namely: reducing sugar (invert sugar), non-reducing sugar (cane sugar), and cane sugar combined with calcium oxide (calcium sucrate). The presence of any appreciable quantity of calcium sucrate does not seem very probable for the reason that *sugar sand* treated with water gives a neutral or acid solution. As previously stated, I have never had a sample which gave an alkaline reaction, and aqueous solutions of the three compounds, which cane sugar forms with calcium oxide, are alkaline.

As a preliminary test for sugar, a weighed quantity of material was mixed with water and allowed to stand for an hour at room temperature. The slightly colored neutral solution was filtered from insoluble matter.

[1] *J. Franklin Institute*, Oct., Nov., and Dec., 1908.

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The filtrate, freed from calcium by means of potassium oxalate solution and filtered from calcium oxalate, gave an immediate reduction when added to boiling diluted Fehling's solution, and consequently contained reducing sugar. Under the conditions an inversion of cane sugar was not possible. Another portion of the same solution was warmed with phenylhydrazine acetate and crystals of an osazone appeared. These crystals under the microscope had the sheaf-like form characteristic of phenylglucosazone and melted at 204°.

Quantitative Determination of Sugars.—The quantity of invert sugar and cane sugar was determined as follows: A weighed amount of *sugar sand* (about 10 grams) was mixed with water and allowed to stand at room temperature with the calculated quantity of oxalic acid required to convert all the calcium into oxalate. After three hours the solution was filtered from insoluble matter which was washed until free from acid. Filtrate and wash water, after neutralization with dry sodium carbonate and filtration, were brought to a volume of 250 cc. The quantity of invert sugar in this solution was determined by titration with a diluted Fehling solution (50 cc. = 0.05 gram of glucose). An aliquot part of this solution, after inversion with hydrochloric acid and neutralization, was again titrated with Fehling's solution. As the result of several determinations, *sugar sand* was found to contain 1.96 per cent. of invert sugar, calculated as glucose; and 3.45 per cent. of non-reducing sugar, calculated as cane sugar.

Examination of Sugar Sand for Sucrate.—Invert sugar and cane sugar are somewhat soluble in 80 per cent. alcohol, whereas compounds of cane sugar with calcium oxide (sucrates) are practically insoluble. A weighed quantity of *sugar sand* (about 100 grams) was extracted three times with 200 cc. portions of boiling 80 per cent. alcohol. The filtered alcoholic extracts were distilled and the thick, sirupy residue treated with cold water and filtered. After removal of some calcium by means of potassium oxalate and filtration, the solution, titrated with Fehling's solution before and after inversion, was found to contain 2.31 per cent. of invert sugar and 3.46 per cent. of cane sugar.

The *sugar sand* extracted three times with 80 per cent. alcohol was tested further for sugar. In one instance it was suspended in water and carbon dioxide was passed through the mixture for several hours. The solution was filtered, freed from calcium, heated with dilute hydrochloric acid on the water bath and brought to a volume of 250 cc. Titration with Fehling's solution gave an entirely negative result. Other tests also failed to show the presence of sugar. These experiments, therefore, show that *sugar sand* contains both invert sugar and cane sugar, but do not indicate the presence of any appreciable amount of sucrate, unless calcium sucrate is slightly soluble in 80 per cent. alcohol.

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A considerable quantity of alcohol was used and it may be that some sugar as calcium sucrate was dissolved. The alcoholic extracts always contained calcium, but I have observed that solutions of the residues from these extracts, when treated cautiously with just enough oxalic acid to precipitate all the calcium, become strongly acid. This would seem to indicate that some calcium malate is dissolved, though of course calcium could be there as sucrate in small quantity.

Ether-Soluble Matter.—A portion of the residue from the alcoholic extract is fatty in character and insoluble in water. This result led to a separate ether extraction of *sugar sand*, 100 grams being treated three times with 200 cc. portions of this solvent. The combined ether extracts had a yellowish color. After distillation of ether, the residue dried to constant weight at 100° amounted to 0.37 per cent.

This fatty material had a yellow color and resembled butter in appearance and odor. Unquestionably it has no connection with *sugar sand* itself. It is the custom among manufacturers of maple products to use a small quantity of some fatty substance, such as butter or pork fat, to prevent the boiling sap from frothing over, and some of this fat, if not all, is carried down by the precipitated *sugar sand*. This fact probably accounts for the presence of this ether-soluble matter.

Carbon Dioxide.—Finely powdered *sugar sand* was treated with dilute sulfuric acid in a Mohr alkalimeter, the evolved gas being displaced by dry air and the apparatus being heated on the water bath during the process. The loss in weight, due to carbon dioxide, was 0.66 per cent.

Extraneous Organic Matter.—*Sugar sand* contains more or less organic matter, which finds its way into the sap during collection and evaporation. The nature of these substances has not been determined. They are colored and, though probably not wholly insoluble in water and dilute acids, are largely so. The clogging of filters, when solutions of *sugar sand* in dilute acids are separated from insoluble matter, may be caused in part by these organic substances.

To determin extraneous organic matter *sugar sand* was treated with sufficient dilute hydrochloric acid to dissolve calcium salts and the insoluble matter, collected on a Gooch crucible and washed with a small quantity of alcohol and ether, was dried at 110°. The residue, which was mainly silica, lost 2.35 per cent. upon ignition.

Summary.

Samples of *sugar sand*, collected in different localities, or in the same locality even under the conditions described, will probably vary somewhat in composition from year to year. But it is believed that this analysis, the individual results of which are here summarized, gives within rather narrow limits the quantities of the several constituents which this material may be expected to contain.

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ANALYSIS.

Silica (SiO_2)	7.74
Phosphoric acid (P_2O_5)	0.05
Ferric oxide (Fe_2O_3)	0.39
Calcium (Ca)	17.16
Magnesium (Mg)	0.03
Moisture	2.60
Malic acid ($C_4H_4O_5$)	51.48
Invert sugar	2.31
Cane sugar	3.46
Ether soluble matter	0.37
Carbon dioxide	0.66
Extraneous organic matter	2.35
Undetermined (by difference)	11.40
	100.00

Isolation of Malic Acid.

To obtain malic acid from *sugar sand*, it is advisable first to prepare acid calcium malate, $Ca(C_4H_5O_5)_2.6H_2O$. On the basis of a calcium content of about 17 per cent. in *sugar sand*, dissolve 27 grams of crystallized oxalic acid in 300 cc. of water and bring the temperature of the solution to 60° on the water bath but not higher, since acid calcium malate at higher temperatures is said to be decomposed into malic acid and neutral calcium malate. Then add 100 grams of *sugar sand* in small portions at a time and heat at 60° on the water bath for an hour. Half of the calcium will be precipitated as calcium oxalate and the other half will pass into solution as acid calcium malate. Filter on a Büchner funnel and wash the precipitate until free from acid. Concentrate filtrate and washings on the water bath, until crystallization begins, and then cool the solution in ice water, stirring constantly to get small crystals. If these crystals are carefully freed from mother liquor by suction, or better by centrifugalization, and washed with a small quantity of cold water, the product will be snow-white. This salt is sufficiently pure for most purposes, but a second crystallization will give a still better product. In one instance, where a special effort was made to determine how much acid calcium malate could be isolated, about 96 per cent. of the theoretical amount was obtained. Obviously in such a case the entire quantity of material was not pure enough for most purposes unless recrystallized.

In preparing malic acid it is advizable to use acid calcium malate which has been at least once recrystallized, and then thoroughly air-dried. A determination of calcium should then be made. Pure acid calcium malate contains 9.66 per cent. of calcium. Dissolve 30 grams of pure oxalic acid in water, heat the solution on the water bath and while stirring pour in gradually a solution of 100 grams of acid calcium malate heated to 60°. Heat on the water bath for some time and test the clear

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solution both for calcium and oxalic acid. If either is in excess, carefully add a small quantity of the solution required to remove it. In this way a solution, free from oxalic acid and calcium, will be obtained. Filter and concentrate the filtrate first on the water bath and then for several days in an air-closet at 100°. The temperature should not go much above that point. Set the vessel containing the fused acid in a vacuum desiccator and upon standing it will gradually solidify to a snow-white, crystallin mass.

St. Louis, Missouri.

[Contribution from the Chemical Laboratory of the University of Michigan.]

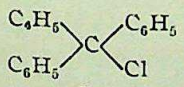
THE ACTION OF HALOGEN ACIDS UPON THE OXYARYL-XANTHENOLS.

[Preliminary Paper.]

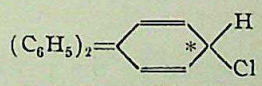
By M. Gomberg and C. J. West.

Received May 24, 1911.

It has been demonstrated[1] that triphenylchloromethane and all its analogues exists in two tautomeric forms: the benzenoid (I) when colorless, and the quinoid (II) when colored. The quinoid compounds behave like salts. In definit solvents they obey the general laws of molecular conductivity; they possess, like all other salts, the capacity to form double salts, to yield perhalides, etc. The salt-like character of these "quinocarbonium" salts was attributed to the carbon atom C*, in so far as it was at all possible to localize upon a single atom in any complex molecule the cause of basicity and of consequent salt-formation.

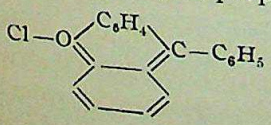


I.

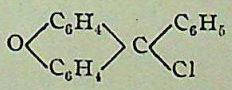


II.

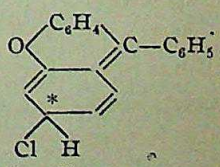
The idea of the quinocarbonium constitution was afterwards extended to the so-called "carboxonium" and "carbothionium" salts—colored compounds obtainable by the action of acids upon xanthenols and thioxanthenols, and to which the constitution (III) had been generally assigned by various investigators, without, however, any direct evidence of an experimental nature. Gomberg and Cone[2] have shown that these xanthenols yield, on proper treatment, absolutely colorless halides. These



III.



IV.



V.

[1] Gomberg, *Ber.*, 40, 1847 (1907); 42, 406 (1909).
[2] *Ann.*, 370, 142 (1909); 376, 183 (1910).

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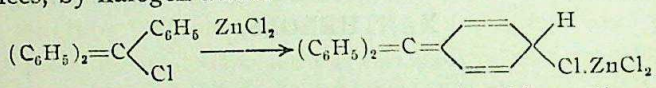
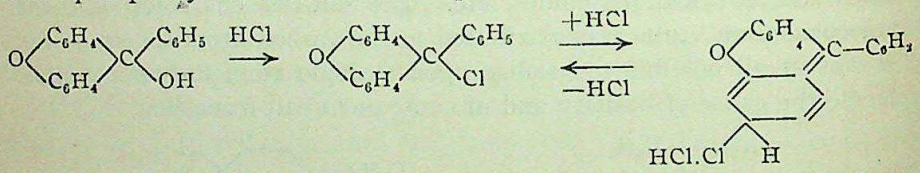
halides were found in every essential characteristic to be true isologues of triphenylchloromethane, and hence the constitution (IV) was assigned to them. The same methods of study that served so well in demonstrating the quinocarbonium structure of the colored triphenylcarbinol salts were applied to the colored xanthenol compounds. The results furnished unmistakable evidence that these colored xanthenol halides are, in reality, quinocarbonium (V) and not "oxonium" salts, the constitution bearing exactly the same relation to the colorless xanthenol halides (IV) as was found to exist in the triphenylmethane series (I and II).

The triphenyl carbinol halides are readily tautomerized to the quinocarbonium salts by means of sulfur dioxide, metallic halides and, in some rare instances, by halogen acids:



The aryl-xanthenol halides (and also those of the thioxanthenols) possess a still more pronounced tendency to tautomerize, and the resulting quinoid salts are decidedly more stable than the corresponding salts of the triphenylmethane series. Halogen acids *very generally* induce this quinoidation in the xanthenol halides, and the resulting acid-salts are frequently only partially decomposed by water. Thus the action of dry hydrochloric acid upon phenylxanthenol can be represented as follows:



The bridge oxygen in the pyrone ring, as has been shown by Gomberg and Cone, possesses, therefore, the double function: first, it imparts to the xanthenol molecule a much greater tendency towards quinoidation than is possessed by the triphenylcarbinol compounds; second, it directs the quinoidation to one of the two phenyl nuclei which are linked to that of oxygen. An examination of the literature[1] shows that oxygen in any form, especially as methoxy or hydroxy groups, universally imparts to the molecule, wherein it is present, a greater tendency to tautomerize to the quinoid state than it might otherwise possess. So pronounced is this influence that polyhydroxy-para-triphenylcarbinols frequently exist only in the quinoid state, although the bridge oxygen is not present in them.

It is, therefore, quite reasonable to presume that the oxyxanthenols are likely to show, when treated with acids, a still greater tendency to tautomerize to the quinocarbonium state than the xanthenols them-

[1] Baeyer and Villiger, *Ber.*, 35, 3019 (1902); Stobbe, *Ann.*, 370, 99 (1909); Gomberg and Cone, *Ann.*, 370, 191 (1909); 376, 211 (1910).

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selves. The action of acids upon aryl-oxyxanthenols has been the subject of numerous investigations.[1] It has been generally reported that they gave rise to colored "oxonium" salts of the constitution (III). We have made a systematic study of this reaction with respect to the oxyxanthenols as an introduction to the study of the constitution of fluoran, fluorescein, hydrochinonphthalein, etc.

Our results, as far as they have gone, differ materially from those reported in the literature. We find: (1) that methoxy- and hydroxyxanthenols, except as specified below under (3), yield *colorless* carbinol chlorides, just like the other xanthenols studied; (2) that these carbinol chlorides tautomerize with extreme readiness to the quinocarbonium salts in the presence of *excess* of acid, forming acid chlorides; (3) that when one of the two phenyl nuclei in the xanthone ring contains a hydroxy group in the *para* position to the carbinol carbon atom, then the normal carbinol halides, even in the absence of excess of acid, tautomerize spontaneously to the colored quinoid state, similarly to the benzo-γ-pyronoles.[2]

In this preliminary paper we shall merely give the results as regards the composition of these colored salts. The method of preparation, the properties of the colorless carbinol halides, their various reactions, the double salts, etc., will be given in a later paper.

The Carbinol-hydrochloride of[3]	Total chlorine. Found.	Calculated Cl_2.	Carbinol chloride.
Phenyl-2-methoxyxanthenol	19.56	19.76	colorless
Phenyl-3-methoxyxanthenol	19.38	19.76	colorless
Phenyl-4-methoxyxanthenol	19.53	19.76	colorless
p-Anisylxanthenol	19.78	19.76	colorless
Phenyl-2-hydroxyxanthenol[4]	20.35	20.56	colorless
Phenyl-3-hydroxyxanthenol	20.32	20.56	yellow, insoluble
Phenyl-4-hydroxyxanthenol[5]	20.41	20.56	colorless
p-Hydroxy-phenylxanthenol	20.38	20.56	colorless

ANN ARBOR, MICH.

THE ADSORPTION OF SOME SUBSTANCES BY STARCHES.

BY HOYES LLOYD.

Received May 20, 1911.

Wolff and Fernbach[6] found that some properties of starch and starch

[1] Baeyer, *Ann.*, 372, 97 (1910); Decker and Fellenberg, *Ann.*, 356, 312 (1907); Kropp and Decker, *Ber.*, 42, 578 (1909); Kehrmann and Dengler, *Ber.*, 41, 3440 (1908); 42, 870 (1909); Kehrmann, *Ann.*, 372, 287 (1910); Pope and Howard, *J. Chem. Soc.*, 97, 1023 (1910); 99, 545 (1911).

[2] Gomberg and Cone, *Ann.*, 370, 196 (1909).

[3] The nomenclature in this table is that given by Richter, *Lexikon* (3rd Ed.); Baeyer (*Ann.*, 372, 98) suggests a different system.

[4] Kropp and Decker (*Ber.*, 442, 578) describe a red chloride. Also Baeyer (*Ann.*, 372, 104).

[5] Baeyer (*loc. cit.*) describes a red chloride.

[6] *Compt. rend.*, 140, 1403–6.

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paste were altered if ordinary lime-containing water instead of distilled water was used for washing the starch. The temperature at which a suspension of starch granules became a translucent liquid was different for the two cases. The viscosity of the paste produced and its acid properties were also different. They say that differences in the properties of the natural starches may be similarly explained.

The properties which Wolff and Fernbach found altered after lime-containing water had reacted with the starch probably indicate that lime had been adsorbed by the starch.

Demoussy[1] treated rice starch, which had been demineralized by dilute hydrochloric acid and washed till it gave no further traces of chlorine, with a number of acid salts, bases, and neutral salts. He found some of the substance removed from solution in every case and concludes that "starch possesses an acid energy comparable to that of carbonic acid and it should act on salts with a facility corresponding to the weakness of their acids." The reactions with bases are also attributed to the acid properties of starch.

It seems more reasonable to consider the loss of a neutral salt such as potassium chloride from solution to be caused by adsorption of that salt.

Apparently, no complete investigation of these adsorption phenomena has yet been made. This paper gives the results of experiments to test the adsorption of three substances, hydrochloric acid, sodium hydroxide and sodium chloride by cassava, arrowroot, potato, rice, and maize starch granules.

Starches Used.

Cassava.—A mixture of three samples sent to the Canadian National Exhibition from the West Indies. Two were from St. Vincent and one from St. Lucia.

Arrowroot.—A mixture of eleven samples from different estates in the West Indies—chiefly from St. Vincent.

Potato.—Supplied by the Edwardsburg Starch Co.

Rice.—This sample was slightly alkaline, as would be expected from the method of preparation—see Jones.[2]

Maize.—The "unchemicalled" brand,[3] manufactured by the Edwardsburg Starch Co. It contained no alkali.

The amount of difference in moisture content of the various starches used was not great enough to cause much variation in results. Moisture determination is entirely arbitrary in the case of starches; hence, the results in the tables are calculated to moist and not to dry starch. The

[1] *Compt. rend.*, 142, 933–5.
[2] Eng. Patent, 1840, No. 8488. Thorpe's "Dictionary of Applied Chemistry."
[3] *J. Soc. Chem. Ind.*, 29, 527–31.

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moisture content determined by heating for two hours averaged 100°, at about 13 per cent.

Method of Operation.

In every case, 50 grams of starch were taken and put to shake with the liquid, which was of known strength and always of 100 cc. volume. Aqueous solutions were used throughout.

The temperature effect seemed to be very slight. At first the shaker was kept in a thermostat at 0°, but this was found to be unnecessary. Practically no difference was observed between points obtained from experiments done at zero and duplicates done at room temperature for maize and for arrowroot starches. Consequently, all experiments were done at room temperature, 20°–24°.

When the liquid has been thoroughly shaken up with the starch, the effect of further stirring was negligible. Thirteen hours' stirring gave only a slightly greater adsorption effect than five minutes' stirring for maize, arrowroot, and potato starch. To insure thorough mixing and to break up any lumps of starch, the bottles were each shaken for five minutes. The rapidity of the reaction in reaching equilibrium points decidedly toward the fact that we are studying a case of simple adsorption.

After shaking, the liquid was separated from the starch and titrated. With starches such as arrowroot and potato, where the granules are large, the suspension settled rapidly and the clear liquid was decanted on a 9 cm. filter paper. The adsorption produced by the filter paper could be neglected, as it was small in comparison to that produced by 50 grams starch. In the case of rice starch, which settles very slowly because of the smallness of the granules, an ordinary centrifuge for milk testing was used. The results produced were the same whether the suspension was settled and decanted, or centrifuged, for centrifuging wide-necked stoppered bottles of about 30 cc. capacity were found more convenient than the ordinary Babcock bottles.

The indicator used for hydrochloric acid and for sodium hydroxide was methyl orange. This was chosen in order to neglect the carbon dioxide present and also because the organic acids present would have least effect on it. Phenolphthalein gave a greater acidity because of carbon dioxide and organic acids and the end point was not so sharp.

The reversibility of the reaction was tested. For example, A was made up thus: 50 grams starch + 60 cc. normal hydrochloric acid; B was made up thus: 50 grams starch + 60 cc. normal hydrochloric acid + 40 cc. water. Then both were shaken for five minutes. Then 40 cc. of water were added to A, which made its total composition the same as that of B. After shaking again, both A and B were centrifuged and the filtrate was titrated. If solution A was weaker than solution B, the

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water had not washed the hydrochloric acid from the starch granules. Solution A was found to be only slightly weaker than solution B, so the reaction may be considered reversible for this concentration. It is doubtful whether this reaction is reversible for starch in solutions of hydrochloric acid weaker than 0.05 normal. Attempts were made at washing the starch free from hydrochloric acid. It is difficult to test the starch for chlorides and so this was abandoned.

In subsequent tables the strength of the equilibrium solution, after the reaction, is given, column I, in normality. The corresponding figures

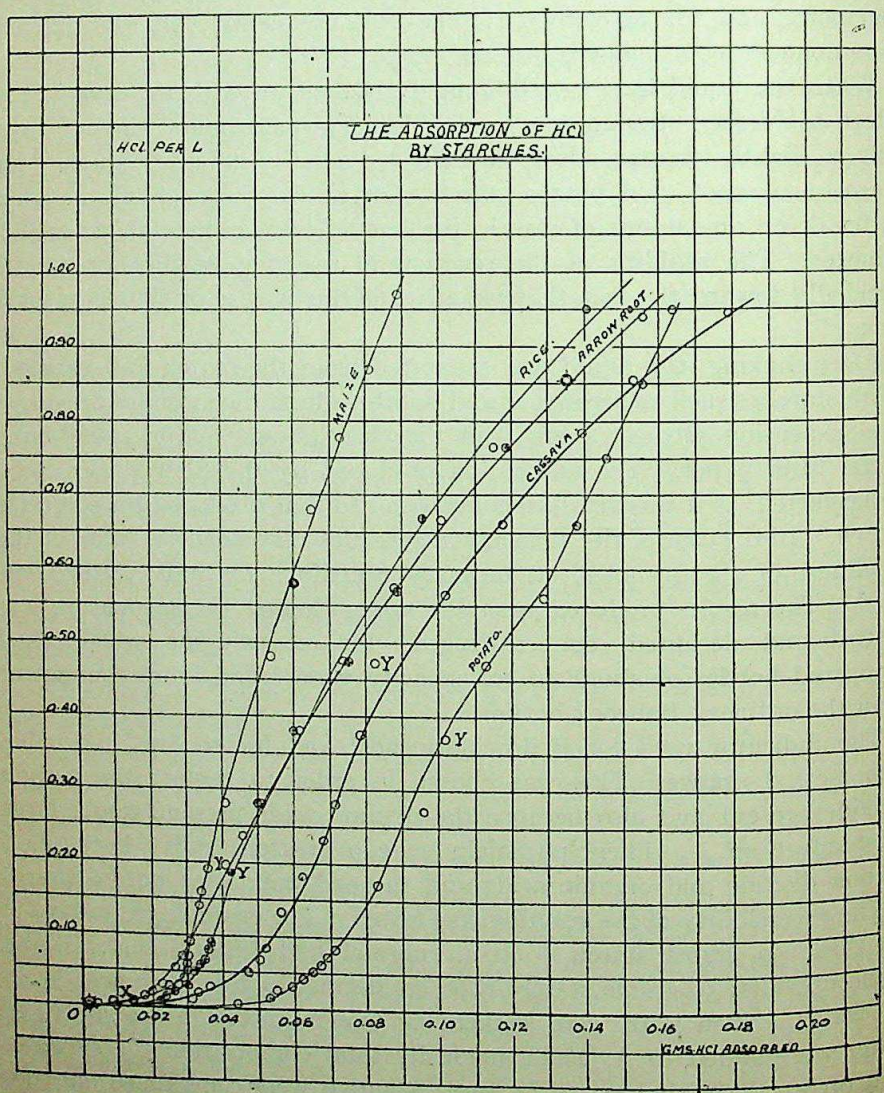

Fig. 1.

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in column II give, in grams, the weight of hydrogen chloride, sodium hydroxide, or sodium chloride adsorbed by 50 grams starch in equilibrium with this solution. The tables and curves (Fig. 1) for hydrochloric acid with starches follow.

Cassava starch-HCl.

I.	II.
Blank	0.0102 g.
0.0013	0.0315
0.0180	0.0340
0.0300	0.0400
0.0469	0.0466
0.0660	0.0495
0.0852	0.0521
0.134	0.0562
0.182	0.0624
0.230	0.0664
0.279	0.0715
0.376	0.0791
0.475	0.0827
0.569	0.102
0.664	0.177
0.758	0.139
0.854	0.153
0.946	0.178

Arrowroot starch-HCl.

I.	II.
Blank	0.0016 g.
0.0072	0.0098
0.0147	0.0188
0.0328	0.0236
0.0521	0.0277
0.0714	0.0294
0.0908	0.0318
0.198	0.0413
0.236	0.0464
0.284	0.0515
0.381	0.0624
0.477	0.0747
0.573	0.0871
0.668	0.101
0.764	0.115
0.858	0.135
0.941	0.156

Potato starch-HCl.

I.	II.
Blank	0.0048 g.
0.0013	0.0314
0.0078	0.0441
0.0152	0.0534
0.0246	0.0551
0.0334	0.0593
0.0425	0.0626
0.0519	0.0647
0.0612	0.0670
0.0705	0.0694
0.0801	0.0709
0.176	0.0834
0.272	0.0961
0.370	0.102
0.466	0.113
0.561	0.128
0.658	0.138
0.756	0.146
0.853	0.155
0.950	0.164

Rice starch-HCl.

I.	II.
Blank	0.0018
0.0085	0.0226
0.0135	0.0231
0.0225	0.0267
0.0318	0.0292
0.0415	0.0300
0.0508	0.0322
0.0604	0.0337
0.0651	0.0348
0.0796	0.0362
0.0893	0.0370
0.187	0.0426
0.284	0.0504
0.381	0.0598
0.477	0.0747
0.572	0.0889
0.670	0.0965
0.763	0.119
0.858	0.135
0.956	0.141

Maize starch-HCl.

I.	II.
Blank	0.0007
0.0056	0.0159
0.0185	0.0206
0.0231	0.0246
0.0320	0.0281
0.0417	0.0290
0.0516	0.0296
0.0614	0.0301
0.0712	0.0305
0.0910	0.0306
0.140	0.0339
0.159	0.0346
0.189	0.0363
0.287	0.0406
0.483	0.0537
0.581	0.0595
0.679	0.0646
0.776	0.0731
0.873	0.0852
0.971	0.0885

The equation $a = k\,c^{p}$ expresses an ordinary adsorption effect where,

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a = amount adsorbed by 50 grams starch.

c = concentration of solution at equilibrium.

k and p = constants.

From this equation

$$\log a = \log k + p \log c$$

which is the equation of a straight line. Since this is the case, if corresponding values for log a and log c were plotted, we should get a straight line as long as the adsorption is following the ordinary law and as long as no other reaction occurs.

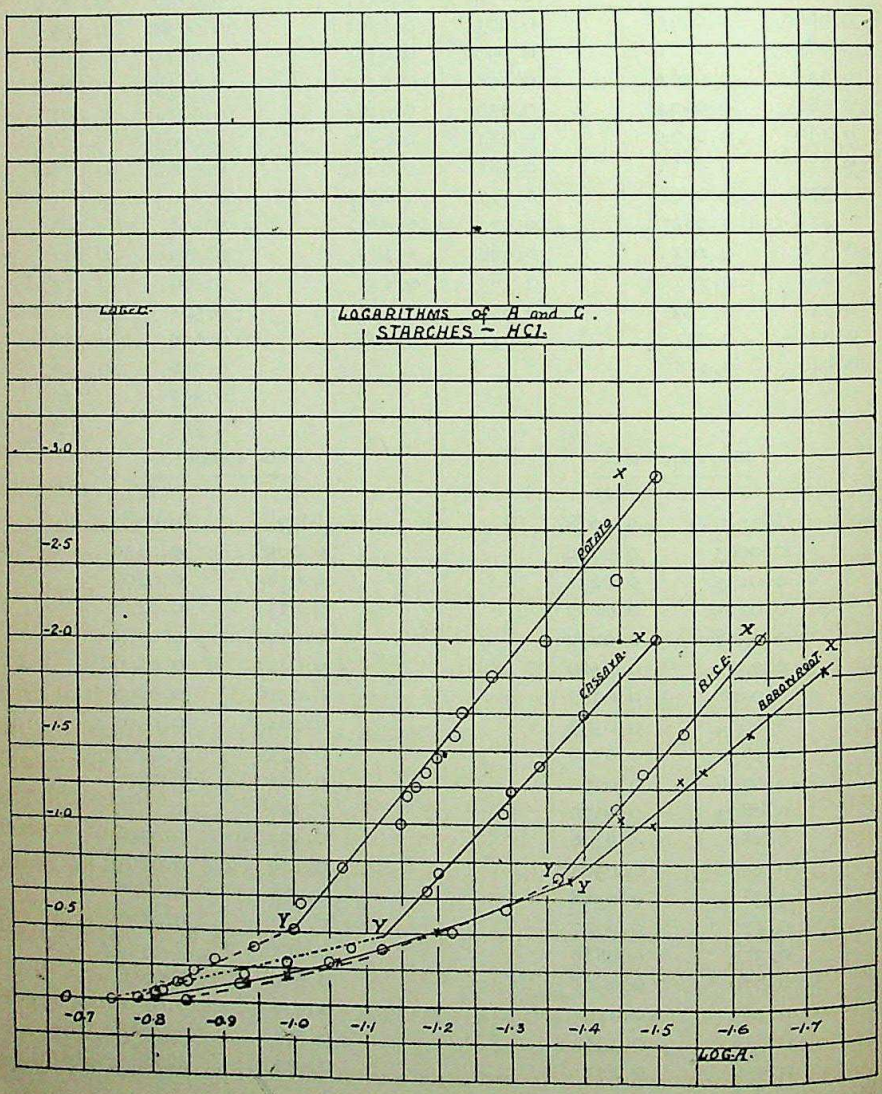

Fig. 2.

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Log a and log c are plotted (Fig. 2) for the various starches with hydrochloric acid. It appears that solutions of hydrochloric acid in which c does not exceed about 0.35 normal are the only ones to obey the above law at all accurately in the case of starches. In Fig. 2 the portion of the curves from X to Y appears to follow the law quite closely.

k and p have been calculated and a solution for the cassava curve follows.

Taking two values for log a and log p,

$$-1.5027 = \log k - 2.0144\,p$$
$$-1.1777 = \log k - 0.6372\,p$$

Subtracting $-0.3250 = \quad -1.3772\,p$

$$p = 0.3250/1.377 = 0.23.$$

Substituting p in one of the above equations,

$$-1.5027 = \log k - (2.914 \times 0.236)$$
$$\log k = -1.031 = \bar{2}.969$$
$$k = 0.093.$$

A comparison of k and p follows:

Starch.	k.	p.
Cassava	0.093	0.23
Arrowroot	0.067	0.30
Potato	0.118	0.20
Rice	0.062	0.21

In general, the adsorption as shown by the starches in Fig. 1 increases rapidly to about 0.04 gram where the equilibrium solution is about 0.05 normal. Then the increase of the amount adsorbed becomes not nearly so large for equal increases in strength of the acid. A slight deviation to the right, above the point 0.05 normal, might be due to a penetration effect, following the ordinary surface effect of the adsorption. If this were so, a shortening of the time of stirring should distinguish it from the adsorption effect, which probably takes place immediately; but, as mentioned previously, the time of stirring did not cause a noticeable variation even when the time was altered from one minute to thirteen hours. The amount of hydrochloric acid adsorption seldom exceeds 6 per cent. of the total acid used when normal solution is put on 50 grams of starch.

The hydrolysis produced by normal hydrochloric acid in the cold and in a period of five minutes is entirely negligible. In case of many hours contact between normal hydrochloric acid and starch, some sugars were produced as indicated by Fehling's solution. Oechsner de Coninck[1] records the time required to produce substances that reduce Fehling's solution. Using 35–40 cc. water, 3 grams starch, and 2 cc. of concentrated

[1] *Bull. acad. roy. Belg.*, 1910, 515–7; *C. A.*, 5, 394 (1911).

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hydrochloric acid, he allowed the reaction to proceed at 14° for three days. Substances that reduced Fehling's solution were found in the liquid after filtration. After six days such substances were found abundantly. Consequently, in these experiments, the amount of hydrolysis is small and so we are dealing with starch granules. As hydrolysis does not remove the hydrochloric acid from solution but uses up starch, its effect would be to lessen, not to increase the adsorption.

The experimental error is large, owing to variation in the 50-gram samples of starch and also to the fact that the amount adsorbed is found by subtracting the amount of the hydrochloric acid after the reaction from the amount in the solution used. Titrations of 50 cc. were used or 50 cc. were diluted to 250 cc. and an aliquot part titrated. The experimental error is greater for the stronger solutions because the amount of the adsorption is small in comparison with the amount of hydrochloric acid present. In these curves, a few points falling a long distance from the curve were rejected as erratic.

Now, adsorption is a surface effect and the amount of the adsorption depends on the surface of the particles. The surface per gram of rice starch is approximately ten times that of potato starch and one would consequently expect greater adsorption effects for rice starch than for the other starches, such as potato starch, which have larger granules and less surface per gram. Potato starch, however, and arrowroot, less notably, have a concentric series of markings which may materially increase the surface of these starches per gram. The starches are dissimilar enough to expect to find differences in the amounts of chemical adsorbed by equal amounts of various starches under similar conditions.

Surface Per Unit Weight.

I have worked out, roughly, the area of surface in 50 grams of three of the starches used. The surface of one granule was calculated, using the average size for the particular kind of starch as given by Archbold.[1] Then the approximate number of granules per gram was estimated by calculating the volume of one granule and using the average specific gravity of starch. The total area for 50 grams is large, as would be expected considering the smallness of the granules.

The equation for the surface of an ellipse was used for potato starch. Where

$$e = \sqrt{a^2 - b^2}/a$$

a and b = half axes.

$$A = 2\pi a b/e \{e\sqrt{1-e^2} + \sin^{-1} e\}$$

The granules of rice and maize were considered spherical although this is not strictly accurate.

[1] *J. Soc. Chem. Ind.*, 22, 63–66.

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Starch.	Area of 1 granule in sq. mm.	Volume of 1 granule in cubic mm.	Diameter of 1 granule in mm.	Area of 50 g. in sq. meters.
Rice	0.0000502	0.0000000335	0.004 × 0.004	49.71
Maize	0.0006408	0.000001532	0.0142 × 0.0142	13.93
Potato	0.002947	0.00001716	0.040 × 0.027	5.99

The Adsorption of Sodium Hydroxide by Starches.

Symons[1] has investigated the process of swelling of starch granules under the action of heat and alkaline solutions of varying strengths. He shows that most granules are swollen and a suspension is converted

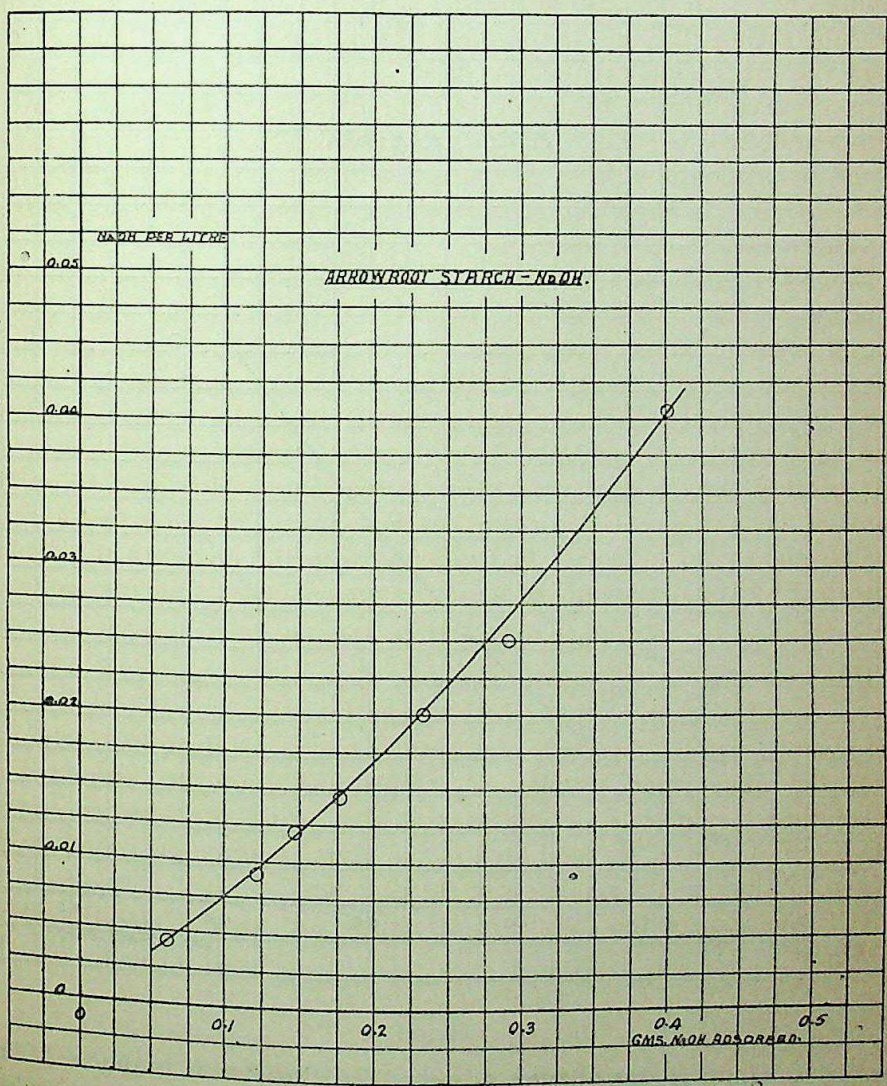

Fig. 3.

[1] Thorpe's "Dictionary of Applied Chemistry," pp. 11[illegible]–562; *Pharm. J. and Trans.*, 3, 13–237.

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into a paste at a point where the solution contains about one per cent. sodium hydroxide.

Brown and Heron[1] state that starch, which has been treated with potash and acid in the process of purification, produces a paste of less viscosity than the same starch which has not been so treated. This is a result

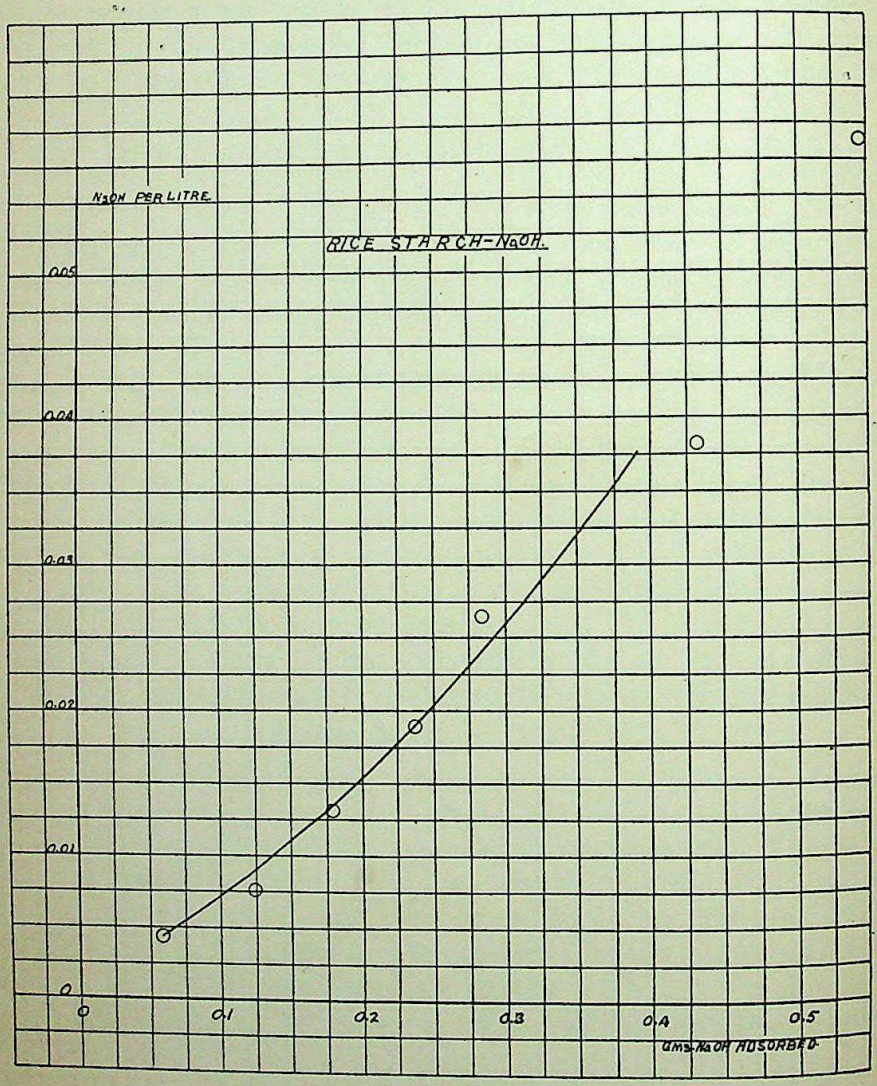

Fig. 4.

probably produced by alkalies adsorbed by the starch granules. They found that when a moderately strong solution of potash or soda was added to an opalescent starch paste, the liquid became perfectly transparent.

[1] *Am. Chem. J.*, 35, 596.

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This fact and the fact that the specific rotatory power is considerably lowered, but resumes its original value if the starch be neutralized, they claim to indicate a definit compound of starch with potash and soda.

In these experiments, concentrations greater than 0.2 normal were not used because the starch gelatinizes with stronger solutions. One

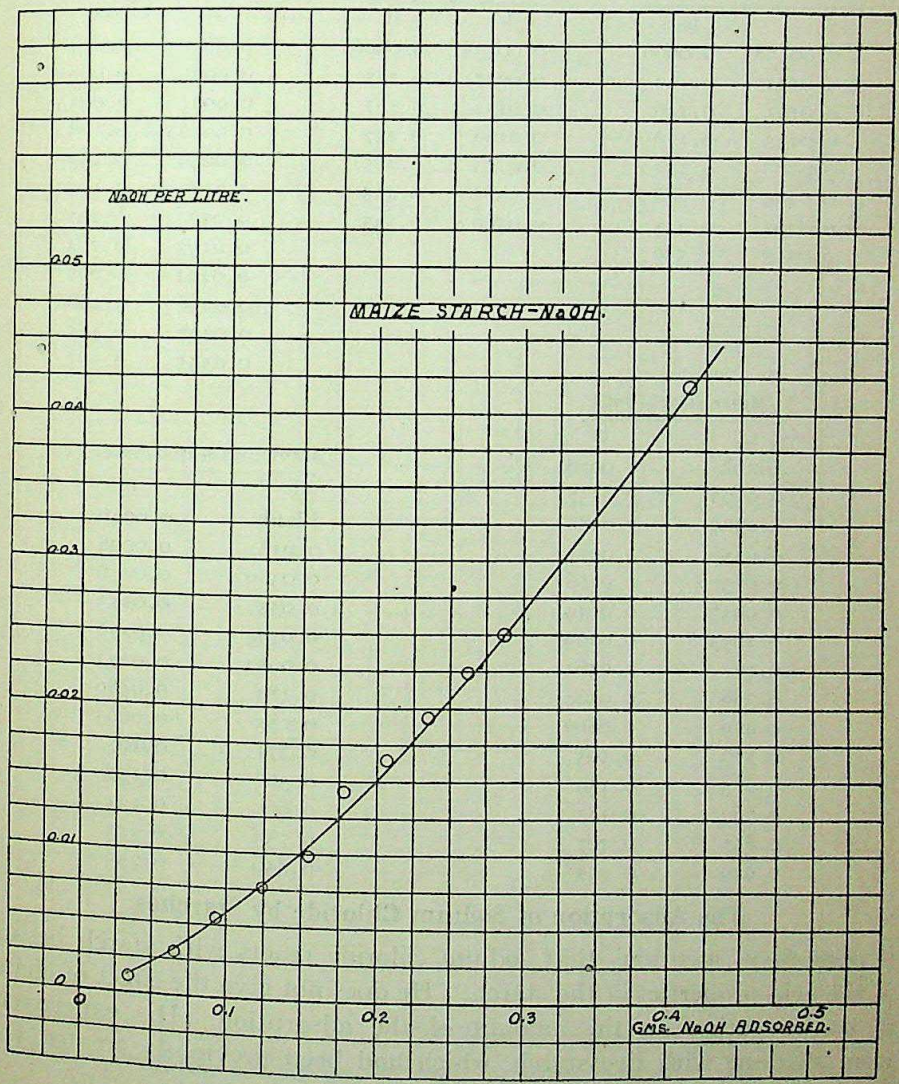

Fig. 5.

minute stirring gave results which compared with thirteen hours' stirring. The equilibrium is reached quickly and is not followed by a penetration effect.

The tables and curves show the experimental results for arrowroot

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(Fig. 3), rice (Fig. 4), and maize starch (Fig. 5). The verticalax is gives the normality of sodium hydroxide in the filtrate after the reaction. The horizontal axis gives, in grams, the amount of sodium hydroxide adsorbed by 50 grams starch. The amount of the adsorption is large in the case of sodium hydroxide.

Arrowroot starch-NaOH.	
I.	II.
0.00438	0.0606
0.0111	0.112
0.0121	0.146
0.0145	0.176
0.0200	0.232
0.0254	0.288
0.0402	0.425
0.0563	0.556

Rice starch-NaOH.	
I.	II.
0.00438	0.0606
0.0077	0.125
0.0132	0.181
0.0188	0.237
0.0263	0.285
0.0382	0.433
0.0589	0.545

Maize starch-NaOH.	
I.	II.
0.0010	0.0347
0.0030	0.0661
0.0054	0.0955
0.0076	0.125
0.0099	0.155
0.0142	0.177
0.0164	0.207
0.0193	0.235
0.0224	0.262
0.0256	0.288
0.0427	0.415
0.0545	0.563

Maize starch-NaCl.	
I.	II.
Blank	0.00294
0.0193	0.0137
0.0364	0.0186
0.0556	0.0218
0.0752	0.0228
0.0947	0.0244
0.1933	0.0269
0.287	0.0561
0.386	0.0584
0.479	0.0862
0.576	0.103
0.665	0.159
0.762	0.185
0.855	0.207
0.949	0.235

Arrowroot starch-NaCl.	
I.	II.
Blank	0.00463
0.0181	0.0098
0.0369	0.0156
0.0557	0.0213
0.0744	0.0276
0.0952	0.0273
0.189	0.0486
0.285	0.0663
0.377	0.107
0.566	0.158
0.660	0.191
0.753	0.223
0.850	0.235

The Adsorption of Sodium Chloride by Starches.

Demoussy[1] mentions that sodium chloride reacts with starch because of the acid properties of the starch. He does not give the effect of change in concentration on the amount of the adsorption. His experiments were all done with rice starch, which had been previously treated with hydrochloric acid.

The solutions were made from Kahlbaum's sodium chloride as it contained no magnesium salts. The sodium chloride in the filtrate after reaction with the starch was determined by titrating with 0.1 *N* silver nitrate solution, using potassium chromate as indicator. The time of

[1] *Compt. rend.*, 142, 953–5.

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stirring was five minutes and the temperature 20°–24°. The results are given for arrowroot and maize starch (Fig. 6). The vertical axis

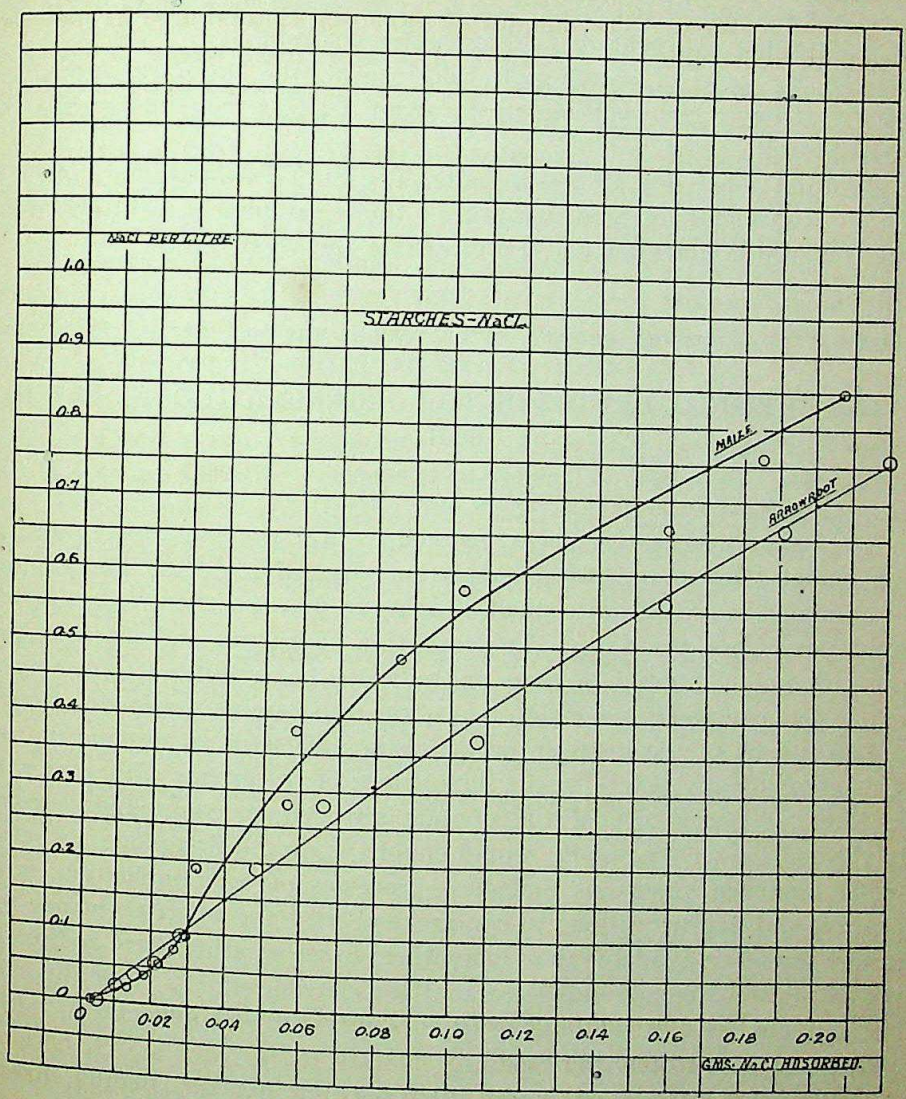

Fig. 6.

gives the normality of sodium chloride after the reaction; the horizontal gives, in grams, the sodium chloride adsorbed by 50 grams starch.

Conclusion.

1. The adsorption of hydrochloric acid, sodium hydroxide, and sodium chloride, by starch, varies with different starches but not as much as would be expected, considering the great differences in the size of the granules.

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2. The adsorption is not a function of the granule surface per unit weight.

3. The amount of the adsorption is much greater for sodium hydroxide than for either hydrochloric acid or sodium chloride.

4. In the case of starch-hydrochloric acid, the ordinary adsorption rule is followed for solutions up to about 0.4 *N*, except in the case of maize starch.

My thanks are due Professor Lang, The Staff in Chemistry, and Dr. W. P. Kaufmann for kind assistance. Some samples were provided by the Imperial Commission on Agriculture for the West Indies.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SOIL, SECTION IOWA AGRICULTURAL EXPERIMENT STATION.]

THE CHEMICAL NATURE OF THE ORGANIC NITROGEN IN THE SOIL.

BY S. L. JODIDI.

Received April 8, 1911.

The data given in this paper, as well as in a previous one,[1] show, in agreement with numerous investigations by others, that the amount of ammonia in soils is quite small, ranging from a few thousands to a few hundreds of one per cent. The proportion of nitrites and nitrates, too, is in the great majority of cases insignificant, being but a few thousands of one per cent. and less, which is true of the soils herein examined. Hence, practically all of the nitrogen occurring in soils is of an organic nature. This emphatically points to the importance of researches with a view to finding out the nature of the organic nitrogenous compounds present in the soil. Such knowledge would enable us, in the first place, to better understand the important biological processes of ammonification, nitrification and denitrification; to comprehend why the nitrogen in one soil is more useful or available than in another; to see whether there are among the nitrogenous compounds such that are detrimental to plant life; and last but not least, it will enable us to utilize the soil nitrogen to better advantage than is now the case.

While some nitrogenous bodies like urea, for instance, readily furnish ammonia through fermentation, others do not. While such compounds like asparagine, *e. g.*, represent plant food, tyrosine is considered as being hurtful to plants, whereas leucine and similar compounds, in the presence of nitrites, can give rise to the process of denitrification, so much so that under favorable conditions leucine is thus quantitatively converted into leucinic acid; other compounds with different chemical structure cannot. Important as is the knowledge of the organic matter in the soil, our pres-

[1] THIS JOURNAL, 31, 396; also *Technical Bull.* 4 (1909), Michigan Agricultural Experiment Station.

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ent scope of information is extremely limited, to say the least. This is very well illustrated by the fact that out of 3794 pages in which Beilstein[1] treats of organic chemistry, but two pages are devoted to humus and humin substances.

In a previous article[2] we have demonstrated that the organic nitrogen in Michigan peat soils is made up of acid amides, monoamino acids and diamino acids. What is true of peat soils must not necessarily hold good for other soil types, for a number of reasons. While peat soils are exceedingly rich in humus and nitrogen, other soil types usually contain a small amount of both of them; whereas the humification process in peat soils, because saturated and oftentimes covered with water, is essentially one of putrefaction taking place in the absence of air, the humification in other soils is one of eremacausis inasmuch as it occurs chiefly in the presence of air.

Further, it will be well to recollect that the method applied for the separation of the organic nitrogenous bodies in peat soils was essentially the Hausmann-Osborne[3] method used in protein chemistry. However, the very assumption that organic nitrogenous compounds occurring in soils can be separated by the same method as applied for protein decomposition products is of a somewhat hypothetical nature and needs direct verification.

The nature of the organic nitrogen in soils being of considerable general interest as well as of paramount importance to agriculture, it may be worth while briefly to show what considerations have led the writer to the above assumption which, it may be said right here, has proved to be correct. Starting from the idea that soil organic matter or humus is the result of decomposed plants, all of which contain a large if not predominant portion of their nitrogen in the shape of proteins, it was but natural to assume the existence in the soil of some disintegration products of proteins. Now, proteins can be split into their constituent parts either by chemical means (*e. g.*, mineral acids or alkalies), or through the activity of certain micro-organisms, or through the agency of enzymes. Of these means the first mentioned is out of the question, inasmuch as even peat soils—the most acid soils known—usually show but a slight acidity largely due to the presence of weak organic acids and acid salts. On the other hand, decomposition of proteins in the soil can and undoubtedly does take place through bacterial activity or the agency of enzymes widely distributed in the vegetable kingdom. Furthermore, disintegration in

[1] See Beilstein's *Handbuch d. org. Chemie*, third edition, first volume, pages 1108–1109.

[2] See "Organic Nitrogenous Compounds in Peat Soils," THIS JOURNAL, 31, 396.

[3] *Z. physiol. Chem.*, 27, 95 (1899); 29, 136 (1900); also THIS JOURNAL, 25, 323 (1903).

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the soil of protein-holding materials into simpler molecules can be accomplished also in a purely chemical way. A. E. Taylor,[1] *e. g.*, has shown that leucine can be recovered from a steril suspension of casein in pure water; he was also able to recover arginine from a solution of protamine sulfate in pure water, after the lapse of about one year. These facts assume considerable significance in processes taking place for a considerable length of time, such as in the soil.

Theoretically, then, the formation in the soil of smaller molecules (amino acids, etc.) out of the various protein compounds contained in decaying vegetable materials seems to be altogether possible and even probable. Nevertheless such deductions as these must be verified by direct experiments as presented in this article. While details will be found in the experimental part, a very brief outline of the questions involved may be given here. The hydrochloric acid extract of the soil was evaporated practically to dryness and distilled with cream of magnesia. The distillate contained, in the form of ammonia, all the nitrogen corresponding to the amides present in the soil. The residue from distillation with magnesia was extracted with water, and the extract, after acidulating with sulfuric acid, treated with PTA.[2] The precipitate contained the diamino acids, and the filtrate from that precipitate represented the monoamino acids.

Now, in the case of proteins proper the distillation of the acid-treated protein with cream of magnesia gives pure ammonia. This, however, may not necessarily hold true for soils recalling that some proteins, through decay, yield organic bases. Thus, methylamine,[3] dimethylamine,[3] and trimethylamine[3] are formed through putrefaction of fish and various protein-holding substances. Likewise decay of organic materials furnishes, under certain conditions, putrescine and cadaverine. Putrescine can also be formed from arginine[4] and ornithine,[5] through bacterial activity, just as cadaverine can result from lysine.[5] Hence, it is not out of the question that the distillation of the acid-treated soil with magnesia may yield, in addition to ammonia, also organic bases. If the distillate contains ammonia only, then it must, when saturated with hydrochloric acid and evaporated to dryness, yield a salt which heated in a test tube will not melt nor be charred, but will sublime. The same

[1] A. E. Taylor, "On Fermentation," Univ. Calif., Publ. Pathol., 1, 223 (1907).

[2] The abbreviation "PTA" will stand for the words: phosphotungstic acid.

[3] *Ber.*, 18, 1922 (1885); 18, 86 (1885); also *Jahresbericht über die Fortschritte der Chemie*, 1858, 231, etc.

[4] *Z. physiol. Chem.*, 43, 338 (1904–5).

[5] *Ibid.*, 29, 334 (1900).

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salt when treated with chloroplatinic acid must yield a compound, the analysis of which is bound to lead to the formula $(NH_4)_2PtCl_6$. This latter salt when decomposed with hydrogen sulfide must give pure ammonium chloride. All of these operations were actually made with positive result, thus showing the presence of ammonia only.

Further, if the PTA precipitate actually contains diamino acids we logically must expect them to show all the precipitation reactions which diamino acids generally display. Moreover, inasmuch as protein hydrolysis leads to α-amino acids of the general type $R.CH.NH_2.COOH$ all of which, with the exception of glycocoll, contain an asymmetric carbon atom, both the diamino acids and the monoamino acids if they be such compounds must, in accordance with the fruitful theory of van't Hoff[1] and Le Bel, be optically active. Furthermore, both must show the presence in their molecules of amino groups as well as of the carboxyl group. The presence of two amino groups in the diamino acids must cause them to show a distinctly alkaline reaction, while the monoamino acids in which one amino group is neutralized by one carboxyl group must show a neutral or slightly acid reaction. And if the NH_2 groups of the amino acids are fixed, *e. g.*, converted into the $—N=CH_2$ group by treating with formaldehyde,[2] then the COOH group must come into play by causing acid reaction, etc. All of the above-mentioned experiments and reactions having as their object the demonstration of the presence of acid amides and amino acids in the soil extracts have actually been carried out with positive results and are given in the experimental part of this paper.

Experimental.

In order to find out the nature of soil humus formed from various organic materials under field conditions the Experiment Station field located on the Wisconsin drift was divided into a number of plots of $^1/_{10}$ or $^1/_{20}$ of an acre each. The various plots were treated with materials like manure, hay, straw, etc., which on cultivated fields actually represent the principal sources for humus formation. For the purpose of rendering the sources of nitrogen in each plot easily reviewable it was thought best to put down the data in question in the form of a table (see Table I).

The percentage of total nitrogen found in the soil samples of the various plots (E, J, Q and U) was as follows: E, 0.278; J, 0.219; Q, 0.263; U, 0.262.

How much of this nitrogen was of organic nature could be answered only after the determination of the inorganic nitrogen has been made.

[1] van't Hoff, *Lagerung der Atome im Raume.* Braunschweig, 1894; also *Ber.*, 18 2277; 20, Ref. 448; 21, 265, etc.

[2] S. P. L. Sörensen, *Biochem. Z.*, 7, 48 (1907).

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TABLE I.—THE SOURCES OF NITROGEN IN THE VARIOUS PLOTS.

Plot.	Treatment (per acre).	Crop.	V.	Remarks.
E	In 1906, a heavy application of manure	In 1906	Corn	The soil samples, the investigation of which is given in this paper, were collected in 1909, at the end of the summer, prior to the treatment of 1909 (which treatment for this reason has been omitted in the table). Each sample is a composite one of 12 or 24 borings taken from each plot at equal distances and equal depth, namely, from the surface down to seven inches depth. The samples collected were dried in the air, passed through a 20-mesh sieve, thoroughly mixed and bottled.
		In 1907	Oats	
	In 1907, one ton of timothy	In 1908	None	
	In 1908, one ton of timothy	In 1909	None	
J	In 1906, a heavy application of manure	In 1906	Corn	
		In 1907	Oats	
	In 1907, two tons of clover hay	In 1908	None	
	In 1908, two tons of clover hay	In 1909	None	
Q	In 1906, a heavy application of manure	In 1906	Corn	
		In 1907	Cow-peas	
	In 1907, no treatment	In 1908	Corn	
	In 1908, no treatment	In 1909	Oats	
U	In 1906, a heavy application of manure	In 1906	Corn	
		In 1907	Oats and clover	
	In 1907, no treatment			
	In 1908, no treatment	In 1908	Corn	
		In 1909	Corn	

The estimation of ammonia was carried out after Schlösing's[1] method slightly modified. The results will be found in Table II.

TABLE II.—PERCENTAGE OF AMMONIACAL NITROGEN IN THE VARIOUS PLOTS.

Plot.	Air-dry soil used. Grams.	Ammoniacal nitrogen found. Grams.	Per cent. of oven-dried soil.	Per cent. of total nitrogen in soil	Moist soil used. Grams.	Ammoniacal nitrogen found. Grams.	Per cent. of oven-dried soil.	Per cent. of total nitrogen in soil.
E	100	0.00261	0.0027	0.99	100	0.00182	0.0022	0.78
J	100	0.00317	0.0033	1.50	100	0.00197	0.0023	1.06
Q	100	0.00317	0.0033	1.25	100	0.00119	0.0014	0.51
U	50	0.00159	0.0033	1.26	100	0.00204	0.0023	0.89

Examining the data of Table II we notice that the figures of the air-dried samples do not agree with those of the moist samples despite the fact that they were simultaneously taken from the soil and prepared for analysis in exactly the same manner. The reason is that between the ammonia estimations of the air-dried samples which were made first and those of the moist samples there was a lapse of from three to five weeks. From the analytical data it is to be concluded that a part of the ammoniacal nitrogen in the moist samples must have changed. It was but natural to suppose, as we did, that the ammonia has been transformed into nitrates in which case the percentage of nitrates in the moist soil samples must be correspondingly higher than in the air-dried samples.

[1] *Technical Bull.* 4 (1909), Michigan Exp. Sta., page 11.

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This supposition has been fully confirmed by the experiment, as can be seen from the data given in Table III.

TABLE III.—PERCENTAGE OF NITRIC NITROGEN IN THE VARIOUS PLOTS.

Plot.	Air-dry soil used. Grams.	Nitric nitrogen found. Grams.	Per cent. of oven-dried soil.	Per cent. of total nitrogen in soil.	Moist soil used. Grams.	Nitric nitrogen found. Grams.	Per cent. of oven-dried soil.	Per cent. of total nitrogen in soil.
E	214.02	0.00227	0.0011	0.40	344.59	0.01729*.	0.0060	2.16
J	264.15	0.00508	0.0020	0.91	418.61	0.02134	0.0060	2.75
Q	246.29	0.00031	0.0001	0.05	335.23	0.00637	0.0022	0.82
U	203.86	0.00026	0.0001	0.05	390.83	0.01312	0.0038	1.46

In looking over Table III we can readily see that the percentage of nitric nitrogen in the moist samples was found to be higher than in the air-dried samples, both calculated to the dry basis. However, by comparing Tables II and III we find that the decrease of ammonia in the moist soils was more than covered by the increase of nitrates in them, the reason being that between the nitrate estimations in the air-dried soils and those in the moist soils several more weeks have elapsed. Besides, it should be borne in mind that the soil samples contained, in addition to ammonia and nitrates, also organic nitrogen which in the moist soil constantly undergoes changes and makes the transformation in question more complicated. Whereas the increase of nitrates in the moist samples in a general way points to conditions in the plots being fairly favorable for the nitrification process, it should be remembered that it is the air-dried samples, the ammonia and nitrate content of which represents the amounts actually present in the soil.

Having ascertained that the sum of ammoniacal and nitric nitrogen is quite small, being but a few thousandths of one per cent. calculated to the oven-dried soils or not quite two per cent. of the total soil nitrogen, the next thing to do was to find a proper solvent for the organic nitrogen in the soils. Water, if it could dissolve out enough nitrogen, would be preferable to either acids or alkalies since it is likely to least change the organic nitrogenous bodies contained in the soils. It is for this reason that water was tried first with the results given in Table IV.

TABLE IV.—EXTRACTION OF SOIL NITROGEN WITH WATER.

Plot.	Air-dry soil. Grams.	Distilled water. cc.	Hours digested.	Nitrogen extracted. Gram.	Per cent. of oven-dried soil.	Per cent. of total soil nitrogen.
E	50	750	10	0.00387	0.008	2.92
J	50	900	21	0.00835	0.017	7.88
Q	50	750	16	0.00768	0.016	6.06
U	40	800	16	0.00751	0.019	7.44

It will be observed that boiling for ten hours was not sufficient to get any appreciable amount of nitrogen in solution. And even boiling

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during twenty-one hours did not dissolve out any considerable quantity, 7.88 being the highest percentage of nitrogen obtained. It was, therefore, decided to use acid for the extraction of soil nitrogen. Preference was given to hydrochloric acid because any excess of it can easily be removed by evaporation. A few preliminary digestions were made to ascertain the optimum conditions for the extraction of nitrogen from the soil samples. The digestions have demonstrated that boiling the soils with concentrated hydrochloric acid for from ten to fifteen hours or with 20 per cent. acid for from twenty to thirty hours extracted the maximum percentage of nitrogen, 83.94 being the highest percentage obtained.

The extraction of the nitrogen from the various soils, as well as its separation into the different organic groups, was accomplished as follows: Four or five or even six round-bottom flasks, each of which contained a mixture of 50 grams air-dry soil and 750 or 900 cc. hydrochloric acid, were heated to the boiling point and kept boiling under reflux condensers for from fifteen to twenty-four hours, depending on the concentration of the acid used. On cooling, the flask contents were made up with water to a definite volume, thoroughly shaken and filtered through dry filters. All of the filtrate or soil extract thus obtained, unless otherwise stated, was used for the experiments in connection with each individual plot.

A portion[1] of the extract, mostly 1000 cc., was evaporated on the water bath practically to dryness and the residue distilled in a 750 or 1000 cc. Kjeldahl flask with cream of magnesia from which every trace of ammonia was previously expelled by long boiling. The distilling substance was absorbed in 0.1 N H_2SO_4. Subtracting from the total ammonia found by titration the amount of ammoniacal nitrogen originally contained in the soil we find the proportion of the amido-nitrogen.

The residue in the Kjeldahl flask was twice extracted with boiling, ammonia-free water being filtered and washed with hot water after each extraction. Filtrates and washings were evaporated on the water bath to 100 cc. and, on cooling to 20°, treated with five grams of sulfuric acid and thirty cc. of a solution containing twenty grams of PTA and five grams of sulfuric acid per 100 cc. After twenty-fours hours the phosphotungstates were filtered out and washed with about 200 cc. of a solution containing 2.5 grams of PTA and 5 grams of sulfuric acid per 100 cc., the washing having been carried out by rinsing the precipitate from the filter into a beaker and returning to the filter three consecutive times. The ammonia resulting from Kjeldahlization of the precipitate represented the nitrogen of the diamino acids present in the soil.

[1] With very few exceptions, all of the estimations given in this paper were made in duplicates and their averages only recorded in the tables.

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Subtracting the sum of ammoniacal, amido, and diamino nitrogen from 100, we find the percentage of monoamino nitrogen. For the sake of convenience the data were arranged in tabular form (see Table V).

TABLE V.—AMOUNT OF NITROGEN IN THE VARIOUS COMPOUNDS.

Plot.		Gram.	Per cent. of oven-dried soil.	Per cent. of total soil nitrogen.	Per cent. of nitrogen in solution.
E	Total nitrogen in solution (obtained by boiling with hydrochloric acid)	0.10380	0.226	81.20	100.00
	Ammoniacal nitrogen	0.00127	0.0027	0.99	1.22
	Nitrogen of acid amides	0.02643	0.0575	20.67	25.46
	Nitrogen of diamino acids	0.01306	0.0284	10.21	12.58
	Nitrogen of monoamino acids (difference from 100)	0.06304	0.1371	49.32	60.74
J	Total nitrogen in solution (obtained by boiling with hydrochloric acid)	0.12795	0.1669	76.23	100.00
	Ammoniacal nitrogen	0.00252	0.0033	1.50	1.97
	Nitrogen of acid amides	0.03435	0.0448	20.46	26.85
	Nitrogen of diamino acids	0.01663	0.0217	9.91	13.00
	Nitrogen of monoamino acids (difference from 100)	0.07445	0.0971	44.36	58.19
Q	Total nitrogen in solution (obtained by boiling with hydrochloric acid)	0.1161	0.1983	75.41	100.00
	Ammoniacal nitrogen	0.00192	0.0033	1.25	1.65
	Nitrogen of acid amides	0.03835	0.0655	24.91	33.03
	Nitrogen of diamino acids	0.01432	0.0245	9.30	12.33
	Nitrogen of monoamino acids (difference from 100)	0.06151	0.1051	39.95	52.98
U	Total nitrogen in solution (obtained by boiling with hydrochloric acid)	0.09312	0.1864	71.12	100.00
	Ammoniacal nitrogen	0.00165	0.0033	1.26	1.77
	Nitrogen of acid amides	0.02858	0.0572	21.83	30.69
	Nitrogen of diamino acids	0.01137	0.0228	8.68	12.21
	Nitrogen of monoamino acids (difference from 100)	0.05152	0.1031	39.35	55.33

Having separated the soil nitrogen into the various groups, the next thing to do was to demonstrate that the groups obtained in the manner described actually represented the acid amides, diamino acids and monoamino acids.

Acid Amides.

Inasmuch as acid amides, by boiling with mineral acids, split off their nitrogen as ammonia, we should naturally expect that the evaporated hydrochloric acid extract of a soil containing amides when distilled with magnesia would give pure ammonia, provided the soil does not contain, in addition to amides, any volatil organic bases. To establish the nature of the distillate the following experiments were carried out:

A definit amount of the soil extract, usually from 1000 to 1500 cc.,

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was evaporated on the water bath to dryness, the residue distilled in a Kjeldahl flask with cream of magnesia, the distillate being absorbed in hydrochloric acid. It was next evaporated to dryness, the remainder taken up with some water whereupon chloroplatinic acid was added and the whole concentrated to syrupy consistency. On cooling, the substance was treated with 80 per cent. alcohol and set aside for a few hours. The chloroplatinate was filtered out, washed with alcohol and dried at 100°. After examining a few crystals under the microscope, a portion of the chloroplatinate was analyzed as to its platinum content. Another portion of it was dissolved in hot water and decomposed with hydrogen sulfide. The filtrate from platinum sulfide was (after decolorizing with animal charcoal, if necessary) evaporated to dryness, and the behavior of the residue observed on heating in the test tube over a burner.

Diamino Acids.

The residues which remained in the Kjeldahl flasks, after the amido nitrogen was expelled with magnesia in the form of ammonia, were thoroughly extracted with ammonia-free hot water, whereupon the extracts were concentrated to 100 cc. and separated by means of PTA into diamino acids (precipitate) and monoamino acids (filtrate) in the manner already described. In order to set free the diamino acids, the precipitate was treated with barium hydroxide and the excess of the latter removed with carbon dioxide when the filtrate from barium carbonate was evaporated to a few cubic centimeters. A small part of the liquid was used for various tests, especially for precipitation reactions, the bulk of it being used for polariscopic examination as well as for estimation of the diamino acids by the formaldehyde titrimetric method.

Monoamino Acids.

The filtrate from the PTA precipitate, supposed to contain monoamino acids, was freed from PTA by means of barium hydroxide, the excess of which was removed with carbon dioxide. The filtrate from barium carbonate was evaporated until crystallization began. On cooling, the crystals were separated by suction from the mother liquor, which on concentration yielded two more crystallizations. All of the crystals proved to consist principally of barium chloride mixed with some potassium and sodium chloride. The mother liquors were separated by suction from the crystals which were treated and washed with alcohol for the removal of organic matter adhering to them. Filtrates and washings were evaporated to a few cc. in order to completely remove the alcohol. The remainder was dissolved in some water, decolored with animal charcoal, filtered, concentrated to a small volume and used for the observation of the rotatory power. It was also analyzed by the formaldehyde titrimetric method. The essential data will be found in Table VI.

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TABLE VI.

Plot.	Acid amides. Behavior in the test tube.	Microscopic examination of the platinochloride.	Analysis of the platino-chloride. % Pt.	Diamino acids. Reactions	Rotatory power (in the 2 dm. tube).	Monoamino acids. Reaction with formaldehyde.	Rotatory power (in the 2 dm tube).
E	The chloroplatinate, it will be recalled, was prepared by the addition of chloroplatinic acid to the distillate which was obtained by distilling the evaporated acid extract of the soil with magnesia.	Examination of the platinochloride crystals, especially under the microscope, showed beautiful yellow, heavy, hard, translucent octahedrons or prisms. This is true of all the plots, with the exception of J, the platinochloride from which was not examined under the microscope.	43.94	The diamino acids (PTA precipitate) extracted from the plots (E, J, Q and U) showed the following reaction: 1. The aqueous solution was strongly alkaline. 2. PTA gave a heavy, white precipitate. 3. Mercuric chloride gave a gray flocculent precipitate, especially in the presence of barium hydroxide. 4. Silver nitrate gave a grayish white precipitate, soluble in excess of ammonia. 5. Phosphomolybdic acid gave a yellow precipitate. 6. On addition of neutralized formaldehyde to the alkaline solution it soon became acid, indicating the presence of carboxyl and amino groups.	E. The rotation of the diamino acid solution, with 0.013 gr. nitrogen, on acidulating with hydrochloric acid, was $\alpha = +0.1$ (Ventzke).	Addition of neutralized formaldehyde to the monoamino acids extracted from each of the soils examined, immediately brought about acid reaction pointing to the presence of carboxyl and amino groups.	E. The rotation of the aqueous solution of the monoamino acids (obtained from about 100 g. soil) was $\alpha = +0.35°$ (Ventzke). On acidulating with hydrochloric acid the same solution showed $\alpha^1 = +1.54°$.
J	The chloroplatinate thus obtained was dissolved in hot water, treated with hydrogen sulfide, the		44.19		J. Not examined.		J. Not examined.
Q	filtrate from platinum sulfide evaporated to dryness and the residue introduced into a test tube. On heating over the Bunsen burner the		43.98		Q. The rotatory power of the diamino acid solution, under conditions similar to Plot E, was $\alpha^1 = +0.17°$.		Q. The aqueous solution of the monoamino acids, under conditions similar to Plot E, showed the rotation $\alpha = -0.30°$. On acidulating with hydrochloric acid, it showed $\alpha = +0.45°$.
U	substance did not melt, but at once commenced to sublime, evolving white fumes which condensed on the cooler parts of the test tube. The sublimate could be driven forwards as heat was applied. It showed all the reactions of pure ammonium chloride. The above observations were made with all the plots.		44.09		U. The rotation of the diamino acid solution, under conditions similar to Plot E, was $\alpha = +0.14°$.		U. The acidulated solution of the monoamino acids, under conditions similar to Plot E, showed the rotation $\alpha = +0.64°$.

[1] The amount of nitrogen contained in the tube could easily have been determined by Kjeldahlizing its content. It was, however, saved for the quantitative determination of the diamino (monoamino) acids by the formaldehyde-titrimetrical method. In addition, it should be borne in mind that estimation of the specific rotatory power was not feasible because of the probable presence of several diamino (monoamino) acids. Here, as in the other cases, it was simply intended to establish the fact as to whether or not the substances in question possess rotatory power.

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Examining Table VI we find that the behavior in the test tube of the evaporated filtrate from platinum sulfide, as well as the microscopic picture of the platinochloride, leaves no doubt but that the substance in question represented pure ammonium chloride. This was also confirmed by the analysis of the chloroplatinates. In all cases the percentage of platinum found was a trifle above 43.91 per cent. of platinum required by the formula $(NH_4)_2PtCl_6$. The presence of an organic base would have diminished the percentage of platinum in the double salt.

The optical activity of the substances examined as well as the presence in their molecules of carboxyl- and amino-groups, as shown by the formaldehyde reaction, establish beyond doubt that they actually are amino acids and diamino acids, the latter being also verified by their precipitation reactions and the alkalinity of their aqueous solutions.

The Formaldehyde Titration Method.

In a series of remarkable articles Hugo Schiff[1] was the first to point to the importance of the reaction taking place between formaldehyde and amino acids. He showed that by means of this reaction the amino function can be separated from the acid function, since the formaldehyde neutralizes the influence of the NH_2 group by converting the atom complex $= C\begin{cases}COOH\\NH_2\end{cases}$ into $= C\begin{cases}COOH\\N:CH_2\end{cases}$. Thus, alanine, *e. g.*, is converted into methylene-alanine according to the equation

$$CH_3.CH\begin{cases}NH_2\\COOH\end{cases} + HCOH = CH_3.CH\begin{cases}N:CH_2\\COOH\end{cases} + H_2O.$$

As a consequence of this reaction amino acids, the aqueous solutions of which are practically neutral, show acid reaction immediately upon the addition of neutralized formaldehyde to their solution. This seemed to indicate that it might, perhaps, be possible to work out a method for the quantitative determination of amino acids. In following up this thought, Schiff studied protein solutions as well as a number of amino acids, like glycocoll, alanine, leucine etc., and succeeded in finding out some of the conditions which are necessary for the separation of the base function from the acid function. Thus, this author has laid the first foundation of the titrimetrical method for the quantitative estimation of amino acids, polypeptides and similar compounds. However, because he has not fully taken into consideration the influence of all reagents present in the above reaction, Schiff has not quite succeeded in working out the exact conditions of rendering the method a quantitative one. It is to Sörensen[2] and his coworkers that we owe the complete elabora-

[1] *Ann.*, 310, 25 (1900); 319, 59, 287 (1901); 325, 348 (1902).

[2] *Biochem. Z.*, 7, 48, 407 (1907); also *Z. physiol. Chem.*, 60, 1 (1909); 64, 120 (1910).

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tion of this method. S. P. L. Sörensen has emphatically pointed out that the reaction

$$\begin{array}{l} CH_3 \\ | \\ CHNH_2 \\ | \\ COOH \end{array} + \begin{array}{l} HCOH \\ \\ \\ KOH \end{array} \rightleftarrows \begin{array}{l} CH_3 \\ | \\ CHN : CH_2 \\ | \\ COOK \end{array} + \begin{array}{l} H_2O \\ \\ \\ H_2O \end{array}$$

is reversible, and that the equilibrium of the system depends upon the quantity of each of the chemicals contained in it. While, for instance, an increase of formaldehyde or of potassium hydroxide (*i. e.*, of hydroxyl ions) will shift the station of equilibrium in the direction from left to right, an increase of the quantity of water is bound to shift the station of equilibrium in the opposite direction. From the above it is evident that, if the reaction is to take place in the direction from left to right as completely as possible, a considerable excess of formaldehyde is to be used, whereas the amount of water must be limited to a certain minimum. For this very reason it makes quite a difference whether the titration is performed with *N* or with 0.1 *N* solutions. The experiments by Sörensen have shown that titration with 0.2 *N* solutions gives the most satisfactory results, and in order to eliminate incidental influences of the individual reagents applied, Sörensen recommends to run simultaneously with the formaldehyde[1] titration of the substance also a check analysis with water, taking pains that the end volumes in both should be approximately equal. He further pointed out that if the titration of amino acids and check analyses is effected to pink color only (first phase), phenolphthalein being used as indicator, then the amount of standard alkali used is smaller than theory requires. Through further titration to distinctly red color (second phase) the analytical data are coming nearer to the theory. And by continuing the formaldehyde titration to strongly red color (third phase), the results obtained very closely approach and in some cases equal the theory. In other words, by titrating to a high enough hydroxyl ion content the results obtained by formaldehyde titration are as accurate as those furnished by most of the common titrimetrical methods.

All of the formaldehyde titrations given in this article were performed in accordance with the principles laid down by Sörensen. The reagents applied were: a one-half per cent. phenolphthalein solution; a formaldehyde mixture[2] made up of 50 cc. of 30 to 40 per cent. formaldehyde and 1 cc. of the above phenolphthalein solution to which mixture 0.2 *N* barium hydroxide was added until a weak pink color was reached.

For each individual formaldehyde titration we used 10, 20 or 30 cc. of the solution to be examined simultaneously with 10, 20 or 30 cc. of

[1] Sörensen uses the shorter expressions: "Formol-titration, formol-titrate" instead of the phrases: "Formaldehyde-titration, etc."

[2] *Biochem. Z.*, 7, 64 (1907).

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boiled distilled water as a check solution. To the solution to be estimated 10 cc. of formaldehyde and enough of 0.2 *N* barium hydroxide was added to obtain a red color. Then a couple cc. more of 0.2 *N* barium hydroxide were allowed to run in for the precipitation of carbonates and phosphates present in the soil. Then it was titrated back with 0.2 *N* hydrochloric acid to weak pink color. The check solution was treated exactly in the same way, *i. e.*, 10 cc. of the formaldehyde mixture were added to it and then so much of 0.2 *N* barium hydroxide as to get on titrating back to pink color with 0.2 *N* hydrochloric acid about the same volume as in the amino acid solution. The addition of one drop of 0.2 *N* barium hydroxide made the check solution turn distinctly red (second phase).

To the solution under examination 0.2 *N* barium hydroxide is added by drops until the red color of the check solution is reached.

Through the addition of two more drops of 0.2 *N* barium hydroxide to the check solution it turns strongly red (third phase). Now to the solution to be examined 0.2 *N* barium hydroxide is added dropwise until just this color has been reached.

Inasmuch as the formaldehyde titration method is quite a new one the desire was natural to find out by personal experience as to whether and to what degree the results obtained by that method are accurate. For this purpose we have prepared from casein, according to the directions given by Hlasiwetz[1] and Habermann, several amino acids among which the formaldehyde titrations of leucine and aspartic acid may be given here.

Leucine.—The preparation repeatedly recrystallized and dried at 100-105° C. yielded 10.67 per cent. N, whereas theory requires 10.70 per cent.

10 milligram-molecules, *i. e.*, 1.3117 grams, were dissolved in 50 cc. 0.2 *N* barium hydroxide and made up with water to 100 cc. Thus, a 0.1 *N* solution was obtained to every 2 cc., of which 1 cc. of 0.2 *N* barium hydroxide was added in advance. The formaldehyde titration of the solution, with phenolphthalein as indicator, yielded the following results: 20 cc., 10 cc. and 30 cc. of the solution of leucine required, after allowing for the blank, 9.7 cc., 4.95 cc. and 14.9 cc. of the 0.2 *N* barium hydroxide corresponding to 97.0, 99.0 and 99.3 per cent. of the theory.

Aspartic Acid.—The aspartic acid, which we have obtained as one of the decomposition products of casein, was carefully recrystallized and then dried at 100–105°. Its nitrogen content was found to be 10.64 per cent. Theory requires 10.55 per cent.

15 milligram-equivalents = 15/2 mg.-molecules (0.9983 g.) were dissolved in 73 cc. 0.2 *N* barium hydroxide and made up with water to 150 cc., so that a 0.1 *N* solution was obtained to every 2 cc., of which 1 cc. of 0.2 *N* barium hydroxide was added in advance. The formaldehyde titrations effected to strong red color (third phase), with phenolphthalein as indicator, as before, gave the following results: 10 cc., 20 cc., and 30 cc. of the aspartic acid solution required after allowing for its blanks, 4.95 cc.,

[1] *Ann.*, 169, 150 (1873).

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10.0 cc. and 15.05 cc. of 0.2 *N* barium hydroxide, corresponding to 99, 100, and 100.3 per cent. of the thing.

We shall now give the results of the formol titrations with the diamino acids and monoamino acids which were obtained from the plots E, J, Q and U. Before doing so, however, it will be well to recall that while the monoamino acids contain in their molecule one carboxyl group and one amino group, the case is different with the diamino acids, as far as the number of amino groups is concerned. Whereas such diamino acids as lysine, diaminoacetic acid and diaminotrihydroxydodecanic acid contain for one carboxyl group two amino groups, histidine and arginine have, in addition to one amino-group, the imidazole ring and the guanidine group respectively. In other words, for one carboxyl group the monoamino acids have in their molecule one nitrogen atom, while lysine, diamino acetic acid and diaminotrihydroxydodecanic acid have two nitrogen atoms, and histidine and arginine three and four respectively. Inasmuch as the existence among the protein products of diaminoacetic acid recognized as such by Drechsel[1] is now very doubtful[2] and the diaminotrihydroxydodecanic[3] acid has been found so far among the decomposition products of casein only, it is probably safe to assume that the diamino acids most likely to occur in soils are histidine, arginine and lysine; and under the assumption that they are contained in soils in about equal proportions, we shall have to calculate three nitrogen atoms for each

TABLE VII.

Plot.	Diamino acids.	Monoamino acids.
E	50 cc. liquid containing 0.024 g. nitrogen extracted from the soil of this plot were subjected to the formaldehydetitration with the following result: (1) 15 cc. substance required 0.85 cc. 0.2 *N* $Ba(OH)_2$. (2) 10 cc. substance required 0.60 cc. 0.2 *N* $Ba(OH)_2$. Average: 50 cc. substance required 2.91 cc. 0.2 *N* barium hydroxide which are equivalent to 0.03259 g. nitrogen (135.8 per cent.) if arginine alone were present; or to 0.02444 g. nitrogen (101.8 per cent.) if histidine only were present. The latter figure will also hold good if, in addition to any amount of histidine, the arginine and the lysine were present in about equal proportions. In other words, in both cases all of the nitrogen classified in Table V as that of diamino acids actually represents diamino nitrogen.	135 cc. liquid containing 0.10541 g. nitrogen were subjected to formaldehyde titration with this result: (1) 20 cc. substance required 5.0 cc. 0.2 *N* $Ba(OH)_2$. (2) 30 cc. substance required 7.7 cc. (3) 10 cc. substance required 2.6 cc. 0.2 *N* $Ba(OH)_2$. Average: 135 cc. substance required 34.50 cc. 0.2 *N* barium hydroxide equivalent to 0.09660 g. nitrogen = 91.64 per cent. This means that 91.64 per cent. of the nitrogen classified in Table V as that of monoamino acids actually represents monoamino nitrogen, the remaining 8.36 per cent. belonging to classes other than amino acids.

[1] *Ber. k. sächs. Ges. Wiss.*, 44, 115 (1892).
[2] *Ber.*, 35, 1378 (1902).
[3] E. Fischer and Abderhalden, *Z. physiol. Chem.*, 42, 540 (1904).

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TABLE VII (*Continued*).

Plot.	Diamino acids	Monoamino acids.
J	The liquid containing the diamino nitrogen was not subjected to formaldehyde titration (having been lost by accident).	40 cc. liquid containing 0.0546 g. monoamino nitrogen were given the formaldehyde titration and required 17.96 cc. 0.2 *N* barium hydroxide equivalent to 0.05029 g. nitrogen equal to 92.11 per cent. In other words, 92.11 per cent. of what is classified in Table V as nitrogen of monoamino acids actually represent monoamino nitrogen.
Q	60 cc. liquid with 0.0305 g. nitrogen were given the formaldehyde titration with this result: (1) 10 cc. substance required 0.5 cc. 0.2 *N* $Ba(OH)_2$. (2) 20 cc. substance required 1.05 cc. 0.2 *N* $Ba(OH)_2$. Average: 60 cc. substance required 3.08 cc. 0.2 *N* barium hydroxide equivalent to 0.03450 g. nitrogen (113.1 per cent.) if arginine only were present; or to 0.02587 g. nitrogen (85.8 per cent.) if in addition to any amount of histidine, the other two, *i. e.*, arginine and lysine, were present in equal proportions.	60 cc. liquid with 0.1310 g. nitrogen were subjected to formaldehyde titration with the following result: (1) 10 cc. substance required 4.14 cc. 0.2 *N* $Ba(OH)_2$. (2) 20 cc. substance required 8.13 cc. 0.2 *N* $Ba(OH)_2$. Average: 60 cc. substance required 24.62 cc. 0.2 *N* barium hydroxide equivalent to 0.06894 g. nitrogen (52.63 per cent.). In other words, 52.63 per cent. of what is classified in Table V as such of monoamino acids actually represent monoamino nitrogen, the remaining 47.37 per cent. consisting of compounds not belonging to the amino acid class.
U	As the result of formaldehyde titration it was found that 65 cc. substance with 0.0203 g. nitrogen are equivalent to 2.27 cc. 0.2 *N* $Ba(OH)_2$ corresponding to 0.02542 g. nitrogen (125.22 per cent.) if arginine only were present; or to 0.01907 g. nitrogen (93.9 per cent.) if in addition to any amount of histidine, the arginine and lysine were present in equal proportions.	65 cc. liquid containing 0.08724 g. nitrogen were subjected to formaldehyde titration with the following result: (1) 10 cc. substance required 1.96 cc. 0.2 *N* $Ba(OH)_2$. (2) 20 cc. substance required 3.77 cc. 0.2 *N* $Ba(OH)_2$. Average: 65 cc. substance required 12.50 cc. 0.2 *N* barium hydroxide which are equal to 0.03500 g. nitrogen (40.12 per cent.). This means that of the nitrogen classified in Table V as such of monoamino acids, 40.12 per cent. actually belong to this class.

carboxyl group found by the formaldehyde titration. The conditions are quite simple with regard to the monoamino acids containing as they do one carboxyl and one amino group, hence by formaldehyde titration with 0.2 *N* barium hydroxide we have to calculate 2.8 milligrams of nitrogen for each cc. of 0.2 *N* barium hydroxide used.

The formaldehyde titration of the diamino acids and monoamino acids extracted from the various soils was carried out exactly in the same manner as that of leucine and aspartic acid, and is presented in Table VII.

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Summary.

The methods described in this publication enable one to extract the bulk of the nitrogen present in the soil, and to separate this nitrogen into the various groups.

All of the organic nitrogen found, by the mode of separation herein described as amido nitrogen, is actually made up of acid amides.

Practically all of the organic nitrogen found as diamino nitrogen actually consists of diamino acids.

Concerning the monoamino nitrogen calculated by difference from 100, it was found that from 40.12 to 92.11 per cent. of what is given in Table V as nitrogen of monoamino acids actually belong to this class of compounds.

The amount of total nitrogen extracted from the soils of the various plots examined, by boiling with hydrochloric acid, was on the average 75.99 per cent. (from 71.12 to 81.20 per cent.), the balance (from 28.88 to 18.80 per cent.) having remained undissolved.

The acid-soluble nitrogen is made up as follows:

Ammoniacal nitrogen, from 1.22 to 1.97 per cent. (from 0.99 to 1.50 per cent. of the total soil nitrogen);

Nitric[1] nitrogen, from 0.07 to 1.19 per cent. (from 0.05 to 0.91 per cent. of the total soil nitrogen);

Nitrogen of acid amides, from 25.46 to 33.03 per cent.;

Nitrogen of diamino acids from 12.21 to 13.00 per cent.;

Nitrogen of monoamino acids from 22.20 to 55.66 per cent.

The rest of the organic nitrogen consists of compounds other than acid amides and amino acids.

By boiling with water, only a small proportion of nitrogen, namely from 2.92 to 7.88 per cent. of the total soil nitrogen, could be extracted from the various soils investigated. This, taken together with the fact that the bulk of the soil nitrogen is made up of acid amides and amino acids all of which are fairly soluble in water, makes it very likely that these compounds are present in the soil not in a free state, but in some kind of combination.

There is a marked difference between the organic nitrogen formed in the soil from comparatively fresh organic materials on the one hand and organic nitrogen formed from comparatively old organic materials on the other. While in the first case (Plots E and J), with the exception of some 8 per cent., the organic nitrogen consists of acid amides, diamino acids and monoamino acids, it contains in the second case (Plots Q and U) a considerable percentage (from 47 to 60 per cent.) of compounds belonging to classes other than acid amides and amino acids.

AMES, IOWA.

[1] The nitric nitrogen was estimated in water extracts.

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[From the Office of Drug Plant, Poisonous Plant, Physiological and Fermentation Investigations, Bureau of Plant Industry, Department of Agriculture.]

THE RELATION OF THE ODOROUS CONSTITUENTS OF CERTAIN PLANTS TO PLANT METABOLISM.[1]

By Frank Rabak.

Received May 9, 1911.

Nature of Plant Odors.—In the vegetable kingdom there occur large numbers of plants possessing peculiar aromatic odors, by means of which the plant may ofttimes be characterized. The substances which impart these peculiar odors to plants do not consist of single compounds but mixtures of a number of compounds in varying proportions. In no instance may the aroma of a plant be ascribed to any one substance. Frequently, however, one constituent is observed to predominate over all others, its odor seemingly standing out by itself from the complex mixture. Usually this constituent attracts attention as the odor bearer of the plant.

Plant odors, owing to their volatility with steam, may be separated from the plants by steam distillation, an essential oil resulting, which bears the natural odor of the plant in a concentrated form. These oils are mixtures of numerous aromatic substances which possess definite chemical composition. The compounds which supply the aroma to plants or to the essential oils may be resolved by classification into several groups of organic compounds, namely, hydrocarbons, acids, alcohols, esters, aldehydes, ketones, oxides, phenols, lactones, and sulfur compounds.

Although all of the groups mentioned contribute to the complex odor of the plants or the volatile oils, usually there exist in the oils compounds which seem to attract one as being especially agreeable and fragrant to the sense of smell. The bearers of these pleasant odors, which are so apparent, even in complex mixtures, may generally be stated as being either ester-like or alcoholic in character.

Esters and Alcohols.—The esters represent a class of constituents which are formed by the interaction of alcohols and acids (esterification), there resulting, by the elimination of water, an *ester*. Almost invariably these esters possess a pleasant odor and convey the characteristic mellowness and fragrance to many of the essential oils. Indeed, a number of volatile oils are valued solely according to the percentage of esters which they contain.

The largest number of pleasant smelling esters are usually found in the oils as formates, acetates or butyrates, the acetic acid esters prevailing.

[1] Read at the Minneapolis meeting of the American Chemical Society. Published by permission of the Secretary of Agriculture.

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The oil of lavender flowers, for instance, owes its agreeable odor to the acetic acid ester of the alcohol linaloöl or to the *linalyl acetate*. The oil is valued according ot the percentage of linalyl acetate which it contains, although the free alcohol, *linaloöl*, also exists in the oil.

In this connection may also be mentioned the methyl ester of anthranilic acid, which imparts the characteristic orange odor to oil of orange flowers. Although present in the oil to only a small extent, the orange odor is entirely due to this ester. This constituent is also present in the very fragrant ylang ylang oil, together with several other esters, among them benzyl acetate and the methyl ester of benzoic acid.

Furthermore, it may be stated peppermint oil, although consisting chiefly of the alcohol menthol, nevertheless owes its agreeable fragrance not to the menthol but to the acetic acid ester of menthol, the *menthyl acetate*. An oil rich in menthyl acetate may readily be detected by means of the smell, so characteristic is the odor of this ester.

Effect of Climatic Conditions upon Certain Plant Odors.—The exact role which plant metabolism plays in the formation and production of esters in the plant is at present not clearly understood. It may be stated with some assurance that during the growth and development of the plant changes are taking place in the form of reactions, an upbuilding of the aromatic constituents gradually resulting. Several conditions may serve to accentuate these reactions within the plant organs, as the effect of the season, the amount of sunshine and cloudiness, heat and cold, and excessive dryness or humidity.

Inasmuch as the odorous constituents of some plant are not constant in quantity in an oil, varying somewhat from one season to another, it seems that the climatic conditions mentioned above may in a measure be responsible for this variability. It is very evident that these conditions exert some effect upon the growth of the plant, either retarding or accelerating it, and consequently assisting in the formation or destruction in the plant of the aromatic constituents.

In order to illustrate more clearly the effect of seasonal changes upon volatile plant constituents, a practical observation will be mentioned.

During August, 1904, there was distilled in South Dakota a quantity of the composit plant, *Erigeron canadensis* or Canada Fleabane, a yield of 0.66 per cent. of volatil oil resulting. The same plant distilled at the same time during 1905 yielded but 0.52 per cent. of oil, while a distillation during August, 1908, produced 1 per cent. of essential oil.

The effect of the seasons or conditions of climate upon the percentage yield of oil is rather striking. The plants in the experiment were distilled in the fresh state, all conditions of distillation being identical.

To further illustrate the effect of climatic changes upon the oil, it may be mentioned in connection with the above experiments, that the quality of the oils was equally as variable as the quantity.

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The percentage of esters and free alcohols (the odorous constituents) in the oils varied as follows:

Oil of Erigeron distilled in 1904, 37.8 per cent. of esters,[1] free alcohols,[1] none.
Oil of Erigeron distilled in 1905, 13.6 per cent. of esters, free alcohols, 8.7 per cent.
Oil of Erigeron distilled in 1908, 22.4 per cent. of esters, free alcohols, none.

The varying quantity of esters in the three oils is remarkably striking, especially in the 1904 and 1905 oils. The presence of 6 per cent. of free alcohol in one oil also suggests the probable effect of the climatic conditions exerted upon the plant during that season.

Another plant which also bears out this point clearly is the *Mentha citrata* or bergamot mint.

The fresh plant distilled September 10, 1907, in full blossom produced 0.37 per cent. of essential oil which by assay indicated 33 per cent. of esters, calculated as acetates of the alcohol linaloöl, $C_{10}H_{18}O$. The same plant, distilled under like conditions September 20, 1908, yielded the same per cent. of oil, but the amount of esters calculated as linalyl acetate was increased to 55 per cent.

It becomes self-evident, therefore, that changes of climatic conditions during the growth of the plants serve as important factors in the production of an essential oil during the life processes of the plant, and assist to bring about chemical changes which have a tendency to alter the constituents in a material way.

Effect of Drying upon Certain Odorous Constituents.—In order to further emphasize the fact that certain plants may undergo noticeable changes with regard to their volatil constituents during growth by responding to changes due to variation in climate, the effect of cutting and drying of a plant was studied.

Equally characteristic variations were observed in the oils distilled from plants cut and dried in sunlight.

In this experiment, the Erigeron herb was used. Parallel to the distillation of the fresh plant in August, 1904, which produced an oil containing 35 per cent. of esters and which disclosed an absence of free alcohols, a quantity of the herb from the same field was collected and dried and then subjected to distillation. The percentage of oil obtained was much less than from the fresh herb. The oil when assayed proved to contain but 18.2 per cent. of esters or approximately only one-half the amount observed in the fresh herb oil. On the other hand, this oil possessed 10.98 per cent. of free alcohol while the fresh herb oil was entirely devoid of alcoholic constituents.

The results observed seem to indicate that possibly during the drying process by the assistance of the enzymes and oxidases contained in the

[1] The esters were calculated as acetates of the alcohol $C_{10}H_{18}O$ and the free alcohols as $C_{10}H_{18}O$.

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plant together with favorable conditions of heat and light, there was effected a partial decomposition of the esters with the formation of alcohols.

Effect of Flowering upon Certain Odorous Constituents.—For the determination of the effect of the flowering of a plant upon the odoriferous components, a series of experiments was carried out. The experiments consisted in the distillation of the fresh plant at three stages of its growth, namely: (1) *Before flowering* or while in budded state, (2) *at flowering*, and (3) *after blossoming* or during fruiting stage.

Only the effect of the successive stages of development upon the esters and alcohols will be considered, although the other constituents and principally the terpenic compounds may also suffer changes in quantity.

The three plants selected are typical of plants in which esters and alcohols play an essential part. The following tabulations will serve to show more clearly a comparison of results, the date of each picking and distillation being given, also the percentage yields of oil in each instance, and finally the percentages of ester and free alcohols:

TABLE A.
Mentha piperita.
Peppermint.

Stage of growth.	Date.	Percentage yield of oil.	Ester content menthyl acetate. Per cent.	Alcohol content free menthol. Per cent.
	1908			
Before flowering	7/22	0.23	9.5	31
Flowering	8/21	0.20	14.5	23.6
After flowering	9/25	0.10	24	34

TABLE B.
Mentha citrata.
Bergamot mint.

Stage of growth.	Date.	Percentage yield of oil.	Ester content calculated as linalyl acetate. Per cent.	Alcohol content calculated as linaloöl (free). Per cent.
	1908			
Before flowering	7/20	0.32	47.6	7.3
Flowering	9/22	0.37	55	7.3
After flowering	10/14	0.22	52	5.5

TABLE C.
Artemisia absinthium.
Wormwood.

Stage of growth.	Date.	Percentage yield of oil.	Ester content thujyl acetate Per cent.	Alcohol content thujyl alcohol (free). Per cent.
	1908			
Before flowering	7/2	0.19	26	14.7
Flowering	7/14	0.18	32.5	11.7
After flowering	8/4	0.10	47.5	12

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In consideration of oil of peppermint (Table A) it becomes obvious at a glance that the yield of oil remains practically unchanged during the first two stages of growth, the third stage reducing the yield about one-half. The percentage of the odorous constituent, menthyl acetate, in the oil increases successively, the oil from the "after flowering" stage being exceedingly and noticeably more fragrant than either of the other oils. The free menthol content, however, does not exhibit the steady increase, varying from 31 per cent. in the oil of stage 1, to 23.6 per cent. in the second, and 34 per cent. in the third oil.

The blossoming of the plant seems to have no effect upon the consumption of esters while a slight diminution of free menthol is observed. This, however, was not permanent as the oil distilled a month later again shows an increase in free menthol as well as menthyl acetate.

Whether the peppermint plant, during the course of its growth from the budding period to the fruiting stage, consumes any of the above-mentioned substances is doubtful. It may be concluded, nevertheless, that the plant after passing into the last stage of development does consume other constituents of the oil, thus leaving an oil richer in both esters and alcohols.

In Table B, the yields of oil from the plant *Mentha citrata* follow a similar course to those of the preceding plant, the first and second stages of growth were nearly identical in yield of oil with a sharp diminution in the third stage (after flowering). The content of ester calculated as linalyl acetate reaches its maximum in the oil distilled from the flowering plant, although the percentage of ester in the oil from the plant after flowering was only slightly decreased. The content of free alcohol in the oils remains the same in oils I and II, whereas oil III discloses a slight lowering.

It would seem from a careful consideration of these facts that the plant *Mentha citrata*, which owes its lavender-like fragrance to the esters present, produces at its flowering stage the maximum quantity of ester, which apparently diminishes but little, even after the plant has entered its fruiting condition. As in the case of the peppermint there may be a slight destruction or consumption of some of the terpenic compounds in the oil during the metabolic processes in the third stage of growth, the esters and alcohol remaining practically unaltered.

In the case of the wormwood plant (Table C) much the same conditions exist. The yields of oils follow the same course as the other plants with a sudden drop in the "after flowering" stage.

The percentage of ester, thujyl acetate, reveals a steady increase from 26–32.5 per cent. to 47 per cent. in the three stages of growth. Again there appears to be little if any consumption of the odoriferous compounds

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by the plant during its advancement, either of the esters or of the thujyl alcohol.

Conclusions.

In general, it may be asserted with some degree of assurance that the odorous constituents, the esters, of the aforementioned oils do not manifestly seem to be affected during fructification of the plant. However, in all cases there does appear to have been a period during the growth and development of the plants when, with the assistance of certain favorable conditions, the chemical processes in the plant transformed some of the basal constituents into esters and corresponding alcohols.

The steady upbuilding of the ester compounds in the plants as the advancement of the plants proceeded is strikingly apparent. The percentages of free alcohols seemingly bear but slight relationship to their corresponding esters or to the life processes of the plant.

That the odorous constituents formed in plants are simply products of excretion formed during the metabolism of the plant, and are of no further use to the plant, seems probable, since the plants do not obviously utilize these stored-up compounds for any special purpose other than a possible means of protection against insect enemies from which most aromatic plants are notably free.

It has been shown how the processes of metabolism in the plants were influenced under varying conditions of climate (different seasons); also the effect of drying, and lastly the effects of budding, blossoming, and fruiting upon the life processes of the plants, resulting in every instance in changes in the aromatic constituents, but in no instance was a decided consumption of the ester or alcoholic constituents observed.

WASHINGTON, D. C.

NEW BOOKS.

Contribution a l'Histoire de la Chimie a Propos du Livre de M. Ladenburg sur l'Histoire du Developpement de la Chimie depuis Lavoisier. Par A. COLSON, Professeur a l'École Polytechnique. Paris: A Herrman et Fils. 1910. pp. 130. Price, 3 francs.

Professor Colson, after expressing his admiration for the historical work of Ladenburg, mentions certain conditions in France which hinder any foreigner from accurately estimating the science of France. He therefore treats of some points in the history of chemistry which in France are thought of more highly than seems to be the case in Germany. The tone of the little book is excellent; read in connection with Ladenburg, to which references are numerous, it will give a helpful and interesting view of the brilliant contributions to chemistry which have been made by the countrymen of Lavoisier.

EDWARD W. MORLEY.

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New Ideas on Inorganic Chemistry. By A. WERNER. Translated from the Second German Edition by EDGAR PERCY HEDLEY. pp. xvii + 268. London and New York: Longmans, Green & Co., Price, $2.50.

On the deck of a steamer in San Francisco Bay during the last summer meeting of the American Chemical Society three advanced students of a Western university engaged the writer in an eager and earnest colloquy over Werner's extension of the valence hypothesis. Replying to a question—"Yes, his book is in our library, but it is in German, and we haven't had the time to dig through it." A frank reply and one which would apply to most of our advanced students and even to many of us engaged in work of instruction. By all such this English edition should be welcomed.

In his preface the translator expresses the hope "that he is thereby making Prof. Werner's book of greater use to them (English-speaking chemists). The book is a veritable mine of suggestions for research on inorganic chemistry, and should the translator bring home to any one the great possibilities of research in this direction, then the translator has attained his desire."

The book is issued in attractive form by the publishers and the translator has done his work well, although occasional sentences leave no doubt that it is a translation from the German. For example, page 212, line 30—"According to the nature of the element which combines with the oxygen of the water molecule is it possible to sub-divide anhydro-acids?" Occasional errors are made in the translation of words, for example, page 58, line 5, "steric hindrance" for steric relations, and page 172, line 11, "granite" for garnet.

The German original is not responsible for the following, page 107, line 24—"which also has *got* a sweet metallic taste;" and page 135, line 10—"for they crystallize differently *to* the other salts."

The reviewer has attempted but failed to find any basis for the several spellings "amin," "amine," "ammin" and "ammine," as for example on pages 38, 39, 217 and 240.

In view of the general use of "ammonium" for the grouping, NH_4, and particularly in view of the old ammonium theory for explaining the construction of metal-ammonia compounds, it is unfortunate that the translator uses the word "ammonium" instead of ammonia in such sentences as occur on page 22, line 27; page 27, line 34; page 30, line 8; etc.

One of the most important terms of classification in the original is "Einlagerungsverbindungen" which is translated "substitution compounds." But the author, in explaining the meaning of the German word, states, page 43, line 28–30 (German edition): "Diese Bindungswechsel kann aber nur dadurch erfolgt sein, dass sich das Ammoniakmolekül zwischen die vorher direkt verbundenen Radikale Co und

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NO_2 *eingeschoben* hat." Plainly intercalation and not "substitution" is intended.

A number of evident errors are noted other than errors of translation, for example, page 55, line 16, "platinum" for copper; page 77, line 2, "nitrite" for nitride; page 162, line 1, "diaquopentammines" for diaquotetrammines; page 174, line 2, in the formula, NO_2 for O_2; page 177, line 10, OH_2 for OH; page 209, line 14, "hydro-compounds" for hydroxo-compounds; and page 266, line 18, "basic acids" for basic salts.

Among the very large number of rather unusual formulas, it is not surprising that several typographical errors have been overlooked in the proof-reading.

All such errors are of minor importance, however, in comparison with the distinct service Dr. Hedley has performed in presenting Werner's views in English, for whether we subscribe to such views or not, the book deserves the title given by the translator in his preface—"a veritable mine of suggestions for research on inorganic chemistry."

CHAS. H. HERTY.

The Elements of Qualitative Analysis. By W. A. NOYES, Professor of Chemistry in the University of Illinois. Sixth edition, revised, in collaboration with the author, by G. McP. SMITH, Associate in Chemistry, in the University of Illinois. 8vo, 131 pp. 1911. New York: Henry Holt and Co.

This excellent manual of qualitative analysis has been very largely rewritten for the present edition, in order to bring it up to date, particularly in view of the fundamental researches of A. A. Noyes and his collaborators. The most important improvements in systematic qualitative analysis, resulting from the work of these investigators, have been incorporated in the book. In addition to these changes in analytical detail, more elaborate discussion of the application of the modern theories of solution and of the laws of equilibrium to analytical reactions are included. Thus, the book shows intelligent appreciation of the two directions in which qualitative analysis has shown its most promising development in recent years—a development demanding greater accuracy, a greater proximation towards quantitative conditions in laboratory methods and more extended attention to the physico-chemical principles underlying reactions. Opinions may differ and one's own judgment hesitate, in deciding on the exact extent to which it would be justifiable to carry, in a given course, the advance in either of these directions: the previous preparation of students, the time, the number and training of instructors and assistants and the differences in the aims of laboratories will make it desirable to give various degrees of time and attention to these phases of the instruction in qualitative analysis; but no one who has observed the results of the old and the new methods of instruction can fail to be impressed with the increased interest and the increased

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stimulus to accurate manipulation and to accurate thinking, which are attending the progress in these two directions. If some instructors wish to delve more deeply, more critically into the theoretical relations than this book does, they still would elaborate, not change, the spirit of the work it maps out: if others would narrow, somewhat, the scope of the analytical ground covered, with a view to emphasizing the training of the analytical habit of thought rather than the breadth of subject matter studied, this manual would lend itself, without difficulty, to such a course. Its well-balanced plan of instruction and its up-to-date character should recommend it to a wide circle of workers.

JULIUS STIEGLITZ.

Organic Chemistry for the Laboratory. By WILLIAM A. NOYES, Professor of Chemistry in the University of Illinois. Easton, Pa.: The Chemical Publishing Co. 291 pp. Price, $2.00.

Professor Noyes states in his preface: "The science of organic chemistry rests, for its experimental foundation, on the preparation, usually by synthetical means, of pure compounds. Without a knowledge, based on personal experience in the laboratory, of the relations involved and the methods which may be used in such preparations, no satisfactory knowledge of the science can be acquired. It has been the purpose of the author in writing this book to classify the most important of the laboratory processes which have been used in the development of the science and to illustrate them by concrete examples."

In following this idea of classification, the book is divided into sixteen chapters. In the first, a description of the methods of organic analysis is given. The second chapter considers the "General Operations," such as fractional distillation, determination of boiling points, melting point, and so forth. The next thirteen chapters are devoted to the preparation of one hundred and twenty-six organic compounds, which are grouped under various heads: thus, hydrocarbons; alcohols and phenols; ethers; aldehydes, ketones and their derivatives; acids; derivatives of acids; hydroxy and ketonic acids; carbohydrates; halogen compounds; nitro compounds; amines; diazo, hydrazo, nitroso and other nitrogen compounds; and sulfur compounds. The final chapter deals with the qualitative examination of carbon compounds.

It is not the intention of the author that the order of the experiments in the book be followed, or that a given student should perform all of them, but rather that the instructor select for, and assign to the student, such preparations as seem best suited to his needs.

Each chapter on the "preparations" is prefaced by an excellent general discussion, although no lengthy discourse on the individual experiments follows the "directions," as is the case in the admirable work of Gatterman. The author evidently thinks that such discussion should come after

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the performance of the experiment, and should be personally attended to by the instructor, a point of view which is shared by the reviewer.

The descriptive material, relative to the setting up of apparatus and the conducting of the experiments, is clear and concise and entirely free from ambiguous phrases. The proof-reading has been very carefully done, and the volume is remarkably free from typographical errors.

LATHAM CLARKE.

Practical Physiological Chemistry. By PHILIP B. HAWK, M.S., Ph.D. Third edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1910. Price, $2.50.

A third edition following so soon after the second is sufficient to show the favor with which this very useful book has been received. The new edition differs from the second, reviewed in THIS JOURNAL, 31, 607 (1909), by certain corrections and by the addition of some new quantitative matter. This is a decided improvement, since a quantitative experiment teaches, as a rule, much more than a qualitative one. The many admirable features of the work and its main defects have been mentioned in the former review. The reviewer uses this work in teaching his classes but finds it advisable to require a good deal more quantitative work and also the isolation, in a fairly pure state of several physiologically important substances.

ALBERT P. MATHEWS.

The Nature of Enzyme Action. By W. M. BAYLISS, D.Sc., F.R.S., Assistant Professor of Physiology, University College, London. Second edition. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1911. pp. 137. Price, 3s. 6d.

The first edition, which was reviewed in THIS JOURNAL, 31, 606, has enjoyed a deserved popularity. The literature references have been brought up to date by the author; a few verbal changes have been made, and the use of the monograph greatly facilitated by the introduction of effective paragraph headings.

Professor Bayliss is now very cautious regarding unconditional acceptance of the doctrine of the extreme specificity of enzymes. He writes: "It is, at the present time, a matter of custom to postulate the existence of a new enzyme whenever some substrate, previously unknown to be attacked by any enzyme, is found to be so attacked, either by a well-known preparation or by a newly-discovered one..... It may be objected that the doctrine of 'lock the key' is unduly neglected, unless the doctrine of specificity is completely acknowledged. It appears, however, that Emil Fischer himself did not intend that his simile should be applied in the extreme way that his successors have applied it. His own experiments were, in fact, not continued for a sufficiently long time to decide whether a particular enzyme might not slowly attack a sub-

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strate differing from that on which it is particularly active. Moreover, it must not be forgotten that there are such things as "master-keys" which are capable of opening several different locks" (p. 118).

Reference is made to the probability (according to Rettger) that the coagulation of the blood is not an enzymatic process in its original significance. The arginase system has been introduced into the list of complex systems, but one finds no mention anywhere of the important group of enzymes acting upon purine compounds. LAFAYETTE B. MENDEL.

The Chemistry of Synthetic Drugs. By PERCY MAY, B.Sc. (Lond.). London and New York: Longmans, Green & Co. 1911. Cloth, pp. 229. Price, $2.25.

That the effect of a medicine on a disease is, in the end, governed by the same laws that govern a test tube experiment will be generally conceded. Also, that fundamentally no reason is seen why the action of quinine on the germ of malaria should not, or at all events could not be formulated with the same precision with which we may express the removal of arsenic from a solution by means of hydrogen sulfide. But, while we may have hope in the future, at the present time our knowledge is hopelessly insufficient. However, a beginning has been made, particularly as regards the relation of the chemical constitution of substances to their pharmacologic action; and this beginning is so interesting, so important, that no chemist can afford to be unfamiliar with the known facts. If the chemist pretends to any knowledge of medicaments, then a thorough acquaintance with the known relation of chemical constitution to pharmacologic effect is of first importance.

The book here under discussion, in the main, is devoted to a consideration of the relation of the chemical constitution of carbon compounds as affected by the introduction of radicles or side chains. In general, it may be considered as an abridged edition to the "Arzneimittelsynthese" of Fränkel and it is to be recommended to all to whom, "Fränkel"—because of its German text—is not available. Those who are familiar with the "Arzneimittelsynthese" will want to read this newcomer in the hope that it may contain information of the things on which the other book was silent—and in this they will not be disappointed.

W. A. PUCKNER.

Alcoholic Fermentation. ARTHUR HARDEN, PH.D., D.SC., F.R.S., head of the Biochemical Department, Lister Institute, Chelsea. Monographs on Biochemistry, edited by R. H. ADERS PLIMMER and F. G. HOPKINS. London, New York, Bombay, and Calcutta: Longmans, Green & Co. 1911. pp. 128. Price, $1.25.

Since the epoch-making discovery of zymase by Buchner, our knowledge of the nature of alcoholic fermentation has made such rapid strides that one can scarcely find a published review of this subject which is in any way adequate or up-to-date. Dr. Harden's lectures are commend-

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able because they present much of the newer work in a form that is not only readable but also stimulating in its suggestions. This effect is in good measure attributable to the author's intimate experimental acquaintance with the chemistry of fermentation. This is seen in the chapters on the two factors now recognized to have a remarkable influence upon the fermentation of sugars, namely, the presence of phosphates and likewise of the indispensable co-ferment or co-enzyme in the liquid.

The monograph reviews the experiments of Harden and Young leading to the conclusion that the addition of a soluble phosphate to a fermenting mixture of hexoses with yeast juice or zymin causes the production of an equivalent amount of carbon dioxide and alcohol. The evidence for the formation of a phospho-organic compound and its nature are discussed, an equation of alcoholic fermentation in which hexose phosphate is formed, being constructed as follows:

$$2C_6H_{12}O_6 + 2PO_4HR_2 = 2CO_2 + 2C_2H_6O + 2H_2O + C_6H_{10}O_4(PO_4R_2)_2;$$
$$2C_6H_{10}O_4(PO_4R_2)_2 + 2H_2O = C_6H_{10}O_6 + 2PO_4HR_2.$$

The role of zymase, hexose phosphate, and the problem of the co-enzyme discovered in boiled yeast juice are discussed. A brief chapter takes up inhibitory and accelerating substances.

The most interesting part, perhaps, is that dealing with those heretofore little understood so-called by-products of alcoholic fermentation. The masterly researches of Felix Ehrlich and others, showing conclusively that the alcohols and aldehydes of fusel oil are in reality derived from amino acids formed by the hydrolysis of proteins present in fermenting mixtures, are described in some detail. Harden points out that this so-called fermentation of amino acids is brought about only by the living yeast in the presence of fermentable carbohydrates. Here we learn how the cell is able to supply itself with indispensable nitrogen.

Other chapters take up the chemical changes in fermentation, especially the lactic acid theory, with the various possibilities of other intermediary products (methylglyoxal, glyceraldehyde, dihydroxyacetone), the mechanism of fermentation, etc., all preceded by an historical introduction telling the story of zymase.

This modern, though incomplete, story of alcoholic fermentation deserves to be read by the biologist as well as the technological chemist, because of the value of the fundamental newer contributions to an appreciation of the mode in which chemical changes are accomplished by living organisms.

LAFAYETTE B. MENDEL.

RECENT PUBLICATIONS.

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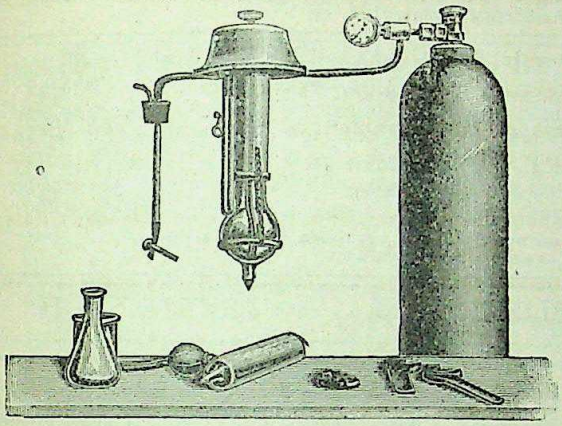

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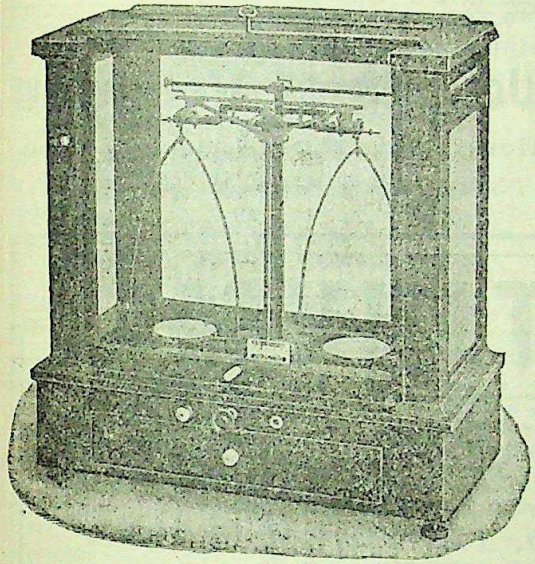

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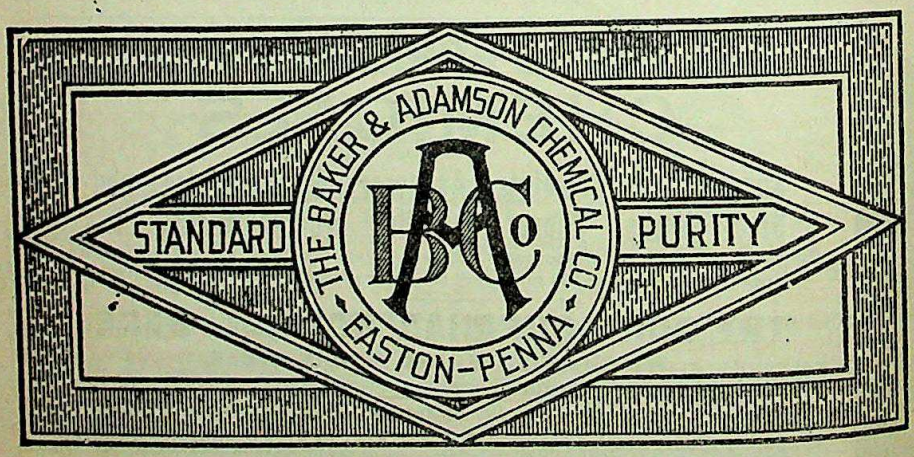

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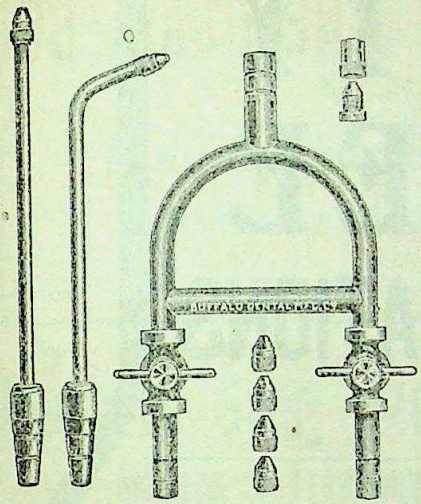

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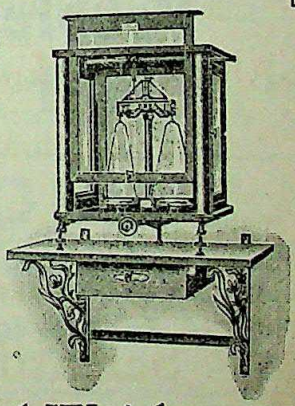

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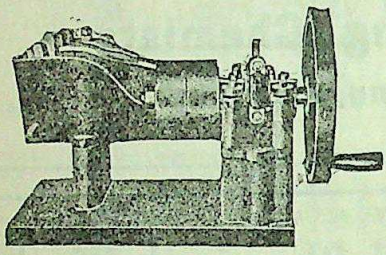

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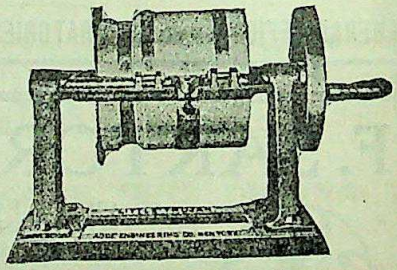

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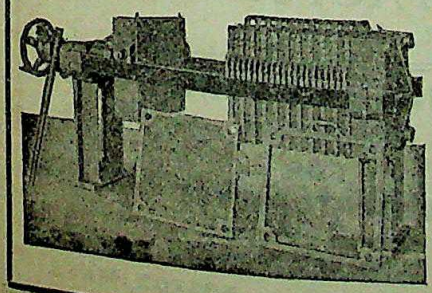

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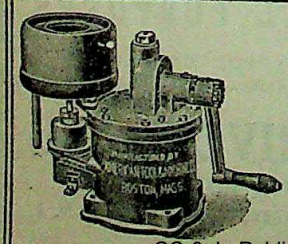

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Proceedings.

MINUTES OF THE FORTY-FOURTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The forty-fourth general meeting of the American Chemical Society was held at the German House, Indianapolis, Indiana, from Tuesday, June 27th, to Saturday, July 1st.

The afternoon and evening of Tuesday were given up to a meeting of the Council interspersed by a recess from 4–8 P.M., which was utilized by an automobil ride to Indianapolis' famous speedway and a complimentary dinner to the members of the Council.

The general meeting was opened on Wednesday morning by President Smith and the following addresses were given:

The Chemistry of Anesthetics. Chas. Baskerville.

The Chemical Philosophy of High School Text-Books. W. Lash Miller.

Report of the Committee on the Quality of Platinum Laboratory Utensils. W. F. Hillebrand.

This latter report was discussed at length in the meeting of the Industrial Division in the afternoon.

Following the papers in the morning a complimentary luncheon was served at the German House.

During the afternoon meetings of the Industrial, Organic, Physical and Inorganic, and Pharmaceutical Divisions were held; also a meeting of the Biological Section.

In the evening at 8 o'clock a complimentary smoker was given to the visiting chemists in the gardens of the German House. The intervals during the smoker were enlivened with amusing lantern slides and vaudeville entertainments of various kinds, some of which were furnished by the members without previous notification. The evening was one of the most thoroughly enjoyable of the whole meeting.

On Thursday, meetings of the Agricultural and Food, Industrial, Organic, Pharmaceutical, and Physical and Inorganic Divisions were held at the German House with the exception of the Pharmaceutical Division, which was given a special outing in the new science hall of Eli Lilly & Co. Following the morning meetings special trolley cars were taken for the inspection of the Indianapolis Brewing Co. and the Eli Lilly & Co. plant, at both of which places complimentary luncheons were extended to the members of the Society. The afternoon was spent in inspecting the plant of Eli Lilly & Co.

In the evening a public lecture, attended by some five hundred people, was given by A. D. Little at the German House on the subject, "The Earning Power of Chemistry." This address will be found published in

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the August number of *The Journal of Industrial and Engineering Chemistry*. Following the address an orchestra concert was held in the gardens of the German House.

Friday morning early a visit was made to the Indianapolis Water Works, following which meetings of the Fertilizer, Industrial, Physical and Inorganic Divisions and the Sections of Biological and India Rubber Chemistry were held.

At 1 o'clock special cars were taken to the automobil factory of Nordyke & Marmon, where a complimentary luncheon was served and the factory inspected.

During the afternoon visits followed to the Encaustic Tile Co., Fairmount Glass Works and E. C. Atkins & Co.

In the evening the usual summer banquet was held at the Columbia Club. Dr. H. W. Wiley acted as toastmaster and the special speakers of the evening were Governor Marshall, of Indiana, and ex-Vice-President Fairbanks.

Saturday was given up to visits to industrial plants, particularly the works of Kingan & Co., the Polk Sanitary Milk Co., Van Camp Packing Co. and the Diamond Chain Co. A complimentary luncheon was served to the members at 1 o'clock, and during the afternoon the members were given a trip to Indianapolis' famous park where bathing and other amusements were enjoyed.

A special program was arranged for the entertainment of ladies so that those who attended the meeting had practically every moment taken up with some enjoyable outing.

Four hundred and thirty-two members and guests were registered.

By motion at the close of the general meeting a unanimous vote of thanks was given to Messrs. H. E. Barnard, H. E. Jordan, R. B. Moore, F. B. Wade, H. A. Schwartz, H. E. Bishop and the members of the committees of which they were chairmen for their strenuous efforts which had made the meeting so great a success, and also to Mr. George Netdwek, of the German House, Mr. Albert Lieber and Mr. Otto Deluse, of the Indianapolis Brewing Co., Mr. J. A. McGowan, of the Indianapolis Street Car Co., Mr. S. O. Dungan, of the Polk Sanitary Milk Co., Mr. J. K. Lilly, of Eli Lilly & Co., the National Candy Co., Indianapolis Water Co., U. S. Encaustic Tile Works, Fairmount Glass Works, Mr. Carl Graf, of the Indianapolis Gas Co., Kingan & Co., Mr. Frank Van Camp, of the Van Camp Packing Co., Mr. H. C. Atkins, of E. C. Atkins & Co., Mr. J. Richard Francis, of the Francis Pharmacy, Mr. W. E. Smith, of the Blue Valley Creamery Co., Dr. L. H. Baekeland, Mr. Thomas Taggart, Governor Marshall, Vice-President C. W. Fairbanks, Mr. Richard Lieber, Nordyke & Marmon Co., Columbia Club, University Club, Commercial Club and Board of Trade, for courtesies extended.

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The programs presented before the various divisional meetings were as follows.

Division of Agricultural and Food Chemistry.

The minutes and program of this Division will be found in the August number of the *Journal of Industrial and Engineering Chemistry.*

Division of Industrial Chemists and Chemical Engineers.

The minutes and program of this Division will be found in the *Journal of Industrial and Engineering Chemistry* for August.

Biological Section.

The Biological Section met for the reading of papers as scheduled on Wednesday afternoon and Friday morning. The attendance was excellent. Although a general feeling of pressure from a full program was felt, a hearty endeavor was in evidence for concise presentation of papers and for pointed and comprehensive criticism in the friendly discussion which followed. Taking into consideration the number and quality of the papers offered and the impartial and ree discussion of the papers in the meetings of the Section, the past history of the Section would seem to indicate the need of such a Section and to augur well for the future. With this in mind, it was moved and passed unanimously by the Section that the Council of the Society be respectfully requested to review the past experience of the Section and to consider the request of the Section to be empowered to form itself into a Division with the rights and privlieges of such a Division of the American Chemical Society. The following papers were presented:

1. The Ash Constituents of Normal and Diseased Cabbage Roots. Howard S. Reed.

2. Effect of Frost on the Aromatic Constituents of the Peppermint Plant. Frank Rabak.

3. The Volatil Leaf-oil of the Washington Cedar, *Thuja Plicata*. Robert E. Rose and Carl Livingstone.

4. Absorption and Excretion of Salts by Roots, as Influenced by Concentration and Composition of Culture Solutions: I. Concentration Relations of Dilute Solutions of Calcium and Magnesium Nitrates to Pea Roots.. R. H. True and H. H. Bartlett.

5. Creatinine in Plants and in the Medium in which they Grow. M. X. Sullivan.

6. The Effect of Temperature on the Respiration of Fruits. H. C. Gore.

7. The Phosphorus Assimilation of *Aspergillus Niger*. Arthur W. Dox.

8. Fermentation and Putrefaction. Arthur I. Kendall.

9. The Carbon Nitrogen Ratio in the Decay of Protein Compounds. Jacob G. Lipman.

10. Biochemical and Toxicological Studies upon Penicillium. C. L. Alsberg and O. F. Black.

11. A Study of the Optical Forms of Lactic Acids Produced by Pure Cultures of *B. Bulgaricus*. James N. Currie.

12. Nucleic Acid in Soils. Edmund C. Shorey.

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13. A Study of Conditions of Tannic Acid Fermentation. Lewis Knudson.

14. The Regulatory Formation of the Enzyme Tannase. Lewis Knudson.

15. The Synthesis of Fats by the Action of Enzymes. F. L. Dunlap.

16. On the Measurement of the Oxidase Content of Plant Juices. H. H. Bunzel.

17. The Pigmentation of the Adult Periodical Cicada. R. A. Gortner.

18. A Study of the Methane Fermentation in the First Stomach of Ruminants. Sleeter Bull.

19. Effects of the Quantity of Protein Ingested on the Nutrition of Animals: II. On the Weight of Some of the Vital Organs of Lambs. W. D. Carroll and A. D. Emmett.

20. Effects of the Quantity of Protein Ingested on the Nutrition of Animals: III. On the Ash and Total Phosphorus of Flesh from Lambs. R. H. Williams and A. D. Emmett.

21. Effects of the Quantity of Protein Ingested on the Nutrition of Animals: IV. On the Creatine of Flesh from Swine and Lambs. W. E. Joseph and A. D. Emmett.

22. A Cage Designed for Metabolism Experiments on Goats. A. R. Rose.

23. On the Lipins of the Heart Muscle of the Ox. Jacob Rosenbloom.

24. The Lipins of the Ovary and Corpus Luteum of the Pregnant and Non-pregnant Cow. Jacob Rosenbloom.

25. Relation of Permeability to the Fertilization of the Ovum. E. P. Lyon and Mr. Shackell.

26. Demethylization under Normal and Pathological Conditions: I. Chronic Alcoholism. Wm. Salant and I. K. Phelps.

27. Elimination of Caffeine in the Urin. Wm. Salant and J. B. Rieger.

28. The Effect of Diet on Resistance to Drugs. Wm. Salant.

29. The Stability of the Photogenic Material of the Lampyridae, and Its Probable Chemical Nature. F. Alex McDermott.

30. Gases of Swiss Cheese. William M. Clark.

31. The Brine-soluble Compounds in Cheddar Cheese. L. L. Van Slyke and A. W. Bosworth.

32. The Influence of Sodium Chloride on the Precipitability of Casein by Acetic Acid, and Its Bearing on the Partition of Nitrogen in Butter. Wm. N. Berg.

33. The Estimation of Creatine. Stanley R. Benedict.

34. The Determination of Calcium in the Presence of Phosphates and Magnesium. F. H. McCrudden.

35. Methods of Estimating Moisture in Tissue. Waldemar Koch.

36. The Preparation of Tissue for Toxicological Examination. (First Part.) James P. Atkinson.

37. Studies of Water Absorption by Colloids. William J. Gies.

38. On the Diffusibility of Biological Substances through Rubber. William J. Gies.

39. The Aging of Flour and Its Effect on Digestion. J. A. Wesener and Geo. L. Teller.

40. The Occurrence of Lipase in the Fat of the Common Fowl, *Gallus domesticus*. M. E. Pennington and J. S. Hepburn.

41. Deterioration in Eggs as Shown by Changes in the Moisture Content. A. D. Greenlee.

42. The Oxidation of Chicken Fat with Hydrogen Peroxide. J. S. Hepburn.

43. Detection and Role Played by Polyatomic Phenols Occurring in Apples as Glucosides. H. P. Bassett.

44. Observations on the Deterioration of Maize and Improvements in the Methods of Detecting It. O. F. Black and C. L. Alsberg.

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45. An Incubator for Moderate Temperatures. A. M. Buswell and Ralph H. McKee.

46. The Absorption of Inorganic Salts by Living Protoplasm. W. J. V. Osterhout.

47. Carbohydrate Esters of the Higher Fatty Acids. Walter R. Bloor.

Division of Fertilizer Chemistry.

The minutes and program of this Division will be found in the August number of the *Journal of Industrial and Engineering Chemistry*.

Section of India Rubber Chemistry.

The minutes and program of this Section will be found in the August number of the *Journal of Industrial and Engineering Chemistry*.

Division of Pharmaceutical Chemistry.

The minutes and program of this Division will be found in the August number of the *Journal of Industrial and Engineering Chemistry*.

Division of Physical and Inorganic Chemistry.

Meetings of the Division were held Wednesday afternoon, Thursday and Friday mornings, Chairman H. P. Talbot presiding. There were forty-four papers on the program, of which thirty-three were presented and eleven were read by title. The list of papers follows:

1. The Mechanism of Reversible Oxidation and Reduction Reactions in Solutions E. P. Schoch.

2. Electrolytic Formation of Aniline without a Diaphragm. E. F. Farnau.

3. Electrolytic Corrosion of Some Metals. G. R. White.

4. The Vapor Density of Formic Acid as Affected by Changes of Temperature and Pressure. Alan W. C. Menzies and Paul N. Leech.

5. The Thermal Expansion of Solid Lithium and Its Change of Volume on Fusion. Alan W. C. Menzies and R. K. Brodie.

6. The Liquidus Surface for the Ternary System Composed of the Nitrates of Potassium, Sodium and Calcium. Alan W. C. Menzies and N. N. Dutt.

7. The Free Energy of Dilution of Hydrochloric Acid. R. C. Tolman and A. L. Ferguson.

8. Note on the Concentration of Hydrogen Ion in Sulphuric Acid. R. C. Tolman and L. H. Greathouse.

9. Estimation of Degree of Ionization in Moderately Concentrated Solutions of Electrolytes. E. W. Washburn.

10. The Dissociation Relations of Caesium Nitrate, Lithium Chloride, and Potassium Chloride in Aqueous Solution at 0°. E. W. Washburn and D. A. MacInnes.

11. Diameters of Pores in Osmotic Membranes. F. E. Bartell.

12. Some Applications of the Electronic Conception of Positive and Negative Valences: IV. Fluorescence. Harry Shipley Fry.

13. Action of Zinc-Copper Couple on Bromoform. Wilder D. Bancroft.

14. Viscosity of Solutions of the Metal-Ammonium Salts. Arthur A. Blanchard.

15. Some New Ammono Salts. E. C. Franklin.

16. Ammonates of Barium Trinitride. A. W. Browne and E. A. Rekate. (Read by A. E. Houlehan.)

17. Ammonated Ammonium Trinitride: A. New Hydronitrogen. A. W. Browne and A. E. Houlehan. (Read by A. E. Houlehan.)

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18. Behavior of Certain Metals in a Liquid Ammonia Solution of Ammonium Trinitride. A. E. Houlehan.

19. Ammonolysis of Certain Hydrazine Salts. A. E. Houlehan.

20. Aluminum Anodes in a Liquid Ammonia Solution of Ammonium Trinitride. M. J. Brown and G. W. Pawel. (Read by A. E. Houlehan.)

21. Note on the Oxidation of Arsenious and Antimonious Oxides by Means of Air. J. Bishop Tingle and Volney A. Ray.

22. The Freezing Points of Liquid Sulphur when *Soufre Nacre* and when Rhombic Sulphur are Deposited. Alexander Smith and C. M. Carson.

23. Crystallized Calcium Tetrasulphide. William McPherson, H. Mougey and James R. Withrow.

24. The Detection of Traces of Copper. A. Guillaudeu, Wesley B. Pritz and James R. Withrow.

25. The Precipitation and Separation of Arsenic Antimony and Tin. J. I. D. Hinds.

26. Reduction of Nitrobenzene by Ferrous Hydroxide. H. C. Allen.

27. The Action of Ammonia on Arsenic Halides. Preliminary Report. C. H. Herty.

28. "Nipponium." Charles L. Parsons.

29. A New Thermostat. Charles L. Parsons.

30. The Hydrolysis of Ethyl Barium Sulphate. W. A. Drushel.

31. The Action of Water on Apatites. F. K. Cameron and W. H. Waggaman.

32. Metallic Properties of Some Organic Radicals. H. N. McCoy, F. L. West and C. H. Viol.

33. Preparation of Anhydrous Perchloric Acid. H. H. Willard.

34. Polyborates. C. L. Parsons and C. O. Brown.

35. The Solubility of Iodine and Potassium Iodide in the Presence of Each Other. C. L. Parsons and C. F. Whittemore.

36. Ozone. Harry N. Holmes.

37. A New Reagent for Potassium. L. L. Burgess and O. Kamm.

38. The Effect of the Magnetism upon the Passive State of Iron and Nickel. Horace G. Byers and Agnes Fay Morgan.

39. A New Method for the Separation of Cerium. Charles James and L. A. Pratt.

40. New Rare Earth Compounds. L. A. Pratt and Charles James.

41. Anhydrous Formic Acid. J. B. Garner.

42. A Convenient Apparatus for the Preparation of Anhydrous Hydrazine. C. F. Hale and F. F. Shetterly. (Read by A. E. Houlehan.)

43. Action of Nitrogen on Lithium Carbide. S. A. Tucker and H. R. Moody.

44. The Separation of Europium. Charles James.

The report of the committee provided for at the Minneapolis meeting to consider, first, the best means of raising about $20–$25 yearly for postage and printing at present paid for by the secretary, and second, to consider the desirability of an addition to the by-laws covering the eligibility of officers to re-election, was presented by the chairman, as follows: First, in view of the fact that other Divisions assess themselves for their current expenses, it seems desirable that this Division should do likewise; second, that no addition be made to the by-laws covering the eligibility of officers to re-election.

Upon motion the report was adopted.

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Upon motion the Division levied an assessment of one dollar per member. The secretary was instructed to collect this amount from those present, and to send out a circular letter requesting payment from those not present, and to keep a record of the names of contributors and amount paid.

The attendance was the largest at a summer meeting in the history of the Division. S. L. BIGELOW, *Secretary*.

Division of Organic Chemistry.

The Division of Organic Chemistry was called together Wednesday at 2.30 o'clock, June 28th, in the German House at Indianapolis. In the absence of Professor Frankforter, the vice-chairman and secretary, Mr. Hale, acted as chairman. The minutes of the preceding meeting, held at Minneapolis, were read and approved. Professor Curtiss made a motion asking for a change in the time of summer meetings of the Society. It was moved and carried that the summer meeting should be made variable and dependent upon the conditions that prevail in the locality selected, and that this question be referred to the consideration of the Society with the support and approval of the Division of Organic Chemistry.

The following twenty-four papers were presented to the Division, two (Nos. 7 and 8) being read by title only. WILLIAM J. HALE, *Secretary*.

1. Derivatives of Isocamphoric Acid. W. A. Noyes and W. T. Murdock.
2. Lauronolic Acid and Other Compounds of the Lauronolic Series. W. A. Noyes, C. E. Burke and R. S. Potter.
3. Decomposition of Nitroso Compounds in the Presence of Alcohols. W. A. Noyes and J. A. Coss.
4. Acyl Derivatives of *o*-Amino-Thiophenol. J. H. Ransom and L. D. Hammond.
5. Ethyl Cyantartronate and Its Addition Reactions and Amines. Richard S. Curtiss and L. F. Nickell.
6. Arsenic and Antimony Derivatives of Certain Organic Acids. J. Bishop Tingle and K. A. Clark.
7. The Action of Halogen Acids upon Oxyxanthenols. M. Gomberg and C. J. West.
8. The Condensation of *p*-Dibrombenzene with Xanthone; a Contribution to the Knowledge of Quinocarbonium Salts. L. H. Cone and C. J. West.
9. The Preparation of Orthotoluquinone and Its Reaction with Hydrazines. William McPherson and Cecil Boord.
10. The Derivatives of Choline. R. R. Renshaw.
11. Determination of Structure from Ionization. Clarence G. Derick.
12. Calculation of Ionization Constants from Structure. Clarence G. Derick.
13. The "Beckmann Rearrangement" of Triphenyl Methylhydroxylamine. J. Stieglitz and G. A. Reddick.
14. A Singular Case of Spontaneous Beckmann Rearrangement. Lauder W. Jones.
15. Three Isomeric Ethyl Normal-propyl Hydroxylamines. Lauder W. Jones and Charles Hecker.

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16. Oxygen Ethers of Cyclic Ureas. Ralph H. McKee.
17. The Constitution of Dehydroacetic Acid. Wm. J. Hale.
18. The Composition of the Resene of *Pinus Heterophylla*. Charles H. Herty.
19. The Action of Carbon Tetrabromide and Organic Bases. Wm. Dehn and A. H. Dewey.
20. The Action of Diiodo Acetylene upon Organic Bases. Wm. Dehn.
21. The Action of Tetraiodo Ethylene upon Organic Bases. Wm. Dehn.
22. The Action of Bromine on Certain Benzhydrols. Latham Clarke and G. J. Esselen, Jr.
23. The Action of Ethyl Magnesium Bromide on Anthraquinone. Latham Clarke and Paul W. Carleton.
24. 2-2-Dimethyl-3-Methyl Pentane. Latham Clarke and W. N. Jones.

COUNCIL.

The Council of the American Chemical Society met at the Claypool Hotel, Indianapolis, Tuesday afternoon, June 27th, at 2.30 P.M., and, with a recess from 4.00 until 8.00, continued into the evening. President Smith presided and the following members were present: G. P. Adamson, E. G. Love, R. R. Renshaw, Alfred Springer, A. M. Comey (for W. T. Taggart), F. C. Phillips, C. H. Herty, W. F. Hillebrand, Edward Bartow, S. W. Parr, W. D. Bigelow, T. J. Bryan (for Wm. Brady, first half of the meeting), Wm. Brady, A. Lowenstein, W. H. McLauchlan (for J. D. Pennock), John White, B. L. Murray, W. Lash Miller, J. O. Handy, C. L. Parsons, Julius Stieglitz, G. D. Rosengarten, Chas. Baskerville, Alexander Smith, S. Calvert, H. P. Talbot, S. L. Bigelow, J. S. Brogdon (for H. B. Arbuckle), W. A. Noyes, W. L. Dudley, E. C. Franklin, H. G. Byers, H. E. Barnard, R. A. Gould (for M. E. Jaffa), J. H. Long, E. H. S. Bailey, A. D. Little.

In view of the fact that the Constitution makes special provision in regard to advance notice to corporate members of papers to be read and of an increasing tendency of members themselves to send in titles after the program has been printed, it was voted that no papers be presented before the general or divisional meetings of the American Chemical Society except such as appear in the final printed program.

It was voted that the Secretary be instructed in receiving the annual reports of treasurers of local sections to request details of expenditures of funds received from the General Society in order that they may be presented to the Finance Committee.

An invitation being read from the Washington Section of the American Chemical Society, inviting the Society to hold its winter meeting for 1911 in Washington, D. C., it was voted that the invitation be accepted with thanks.

A letter from Dr. Bernhard C. Hesse, Secretary of the Eighth International Congress of Applied Chemistry, was presented to the Council,

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requesting the full co-operation of the American Chemical Society toward the success of the international meeting. In view of this communication it was voted that a committee of three on co-operation of the American Chemical Society with the Eighth International Congress of Applied Chemistry be appointed by the Chair, and it was further voted that the question of the summer meeting of 1912 be left to the President and the Secretary, with power, the general idea being that the meeting as a whole be omitted. President Smith appointed Charles Baskerville, C. L. Parsons and G. D. Rosengarten as the Committee on Co-operation.

A letter from Professor Wilhelm Ostwald, President of the International Association of Chemical Societies, was read to the Council, inviting the American Chemical Society to become a member of the International Association representing the United States. After lying on the table for a few hours pending discussion, it was voted, on motion of Past President J. H. Long, that the American Chemical Society views with favor the proposal to join with the chemical societies of London, France and Germany in the formation of an international association on the lines suggested in the provisional program forwarded by Professor Ostwald, and the President of the American Chemical Society is hereby empowered to enter into correspondence on the details of the proposed organization.

The report of the committee formed to consider the question of establishing a journal of agricultural and food chemistry was presented by means of a letter from the chairman. The report was to the effect that there was no unanimity of opinion among the agricultural and food chemists of the country and that it appeared to be the general opinion of the committee that in view of the fact that there was some prospect of the establishment of a federal journal along similar lines, the committee be discharged and that the articles be printed in both of the Society's journals according to their specific character. It was further recommended that Dr. C. A. Browne be added to the editorial board of both journals. After careful consideration, it was voted that the agricultural and food papers be published as heretofore in the two journals of the Society, as indicated by the character of the papers, and that Dr. C. A. Browne be added to the board of editors of each journal to aid in passing on papers bearing upon agricultural or food chemistry. It was further voted that the report as presented by the chairman be accepted and the committee discharged.

A letter from Editor Whitaker in regard to the question of further development of the Industrial Journal and funds therefor was referred to the Directors of the Society with power.

A letter received from A. M. Patterson in regard to the need of further funds for *Chemical Abstracts* was carefully discussed and estimates presented by the Finance Committee. It was voted that the Council ap-

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prove the policy of complete representation of all articles of professional interest to chemists in *Chemical Abstracts;* that *Chemical Abstracts* be kept within the limits set by the appropriation by reduction in the length of abstracts, special reference being had to the accessibility of the journals in which the articles appear, and that the matter of necessary addition to the appropriation be left to the Directors of the Society with power.

Professor H. G. Byers presented an invitation for the Society to meet in Seattle in the summer of 1915. As this could not be constitutionally acted upon until within one year previous to the meeting, it was laid upon the table until that time.

A report of progress by the Committee on Endowment was received from its chairman, Mr. B. T. Babbitt Hyde. The recommendation of the committee that its membership be enlarged to include Arthur L. Day, W. L. Dudley, A. D. Little, E. G. Love, I. K. Phelps, and Theodore B. Wagner was approved.

It was voted that the Committee on Water Analysis be enlarged to five members and be subject, as all other committees, to final approval of their report by the Committee on Standard Methods of Analysis. The President appointed J. H. Long, chairman, W. P. Mason, H. E. Jordan, E. H. S. Bailey and Edward Bartow as the official committee.

On motion of W. F. Hillebrand it was voted that the President be authorized to name a successor to N. W. Lord, deceased member of the Committee on Coal Sampling and Analysis, to increase the membership if such increase shall seem to him desirable, and that he be instructed to name the chairman of the committee.

The committee, consisting of the President and the Secretary, appointed at the Minneapolis meeting to consider the question of the extent of territory to be allowed local sections and also to consider the question of decreasing the size of the Council, presented a somewhat lengthy report based upon communications received from most of the local sections in regard to their ideas on the subject. This report favored the reduction of the size of the Council and the limitation of the apportionment of funds and councilor representation to a basis of residence within a radius of fifty miles of some central headquarters, although membership in the section might be allowed outside this radius. The full report was spread on the minutes of the Society, but as only portions of it met the approval of the Council, those alone are included here. Under this report it was voted:

1st. That territory be dependent on local conditions as voted by the Council and subject to change by the vote of the Council as occasion may require; that members finding it more convenient to attend the

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meetings of a section other than the section in whose territory they reside may choose the section in which they desire to be enrolled.

2d. That the apportionment of funds be placed on the following sliding scale:

Sections having less than 50 members, provided that a minimum of $50 be allowed to any section, not exceeding $1.50 per member.

Sections having not less than 50 members nor more than 125, not exceeding $1.25 per member.

Sections having not less than 125 members nor more than 200, not exceeding $1.00 per member.

Any section having 200 or more members, not exceeding $0.75 per member.

Provided that any section may claim and receive the maximum total amount payable to a section in the class next below it in membership. Expenditure of funds to be limited to necessary expenses as heretofore and local treasurers to report detailed expenditures to the Secretary of the Society in order that they may be passed upon by the Finance Committee.

3d. That the Secretary be instructed to formulate the necessary changes in the Constitution required to carry these provisions into effect; that the changes so formulated, after receiving the approval of the President and Directors, be submitted for ballot by the members of the Society as required by the Constitution.

It was voted to enlarge the territory of the Washington Section to include the State of Virginia.

It was voted to enlarge the territory of the Section of Western New York from a radius of thirty miles to a radius of fifty miles.

It was voted that in determining the basis of councilor representation of any section the representation be based upon the total paid membership of that section of the year preceding.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary*.

MEMBERS ELECTED BETWEEN JUNE 15TH AND JULY 15TH.

Anaconda Copper Mining Co., Boston & Montana Reduction Dept., Great Falls, Mont.

Bitting, Arvill W., Bur. of Chemistry, Lafayette, Ind.

Breitstadt, John H., 325 So. 9th St., Quincy, Ill.

Browne, H. R., Wyandotte, Mich.

Campbell, Frederick A., Director, Working Men's College, Melbourne, Australia.

Chu, V. G., 5642 Ellis Ave., Chicago, Ill.

Cockerill, Samuel, cr. Citizens Gas Co., Indianapolis, Ind.

Connell, Wm. B., Stillwater, Okla.

Craven, Jay, State Board of Health, Indianapolis, Ind.

Cudahy Packing Co., 111 West Monroe St., Chicago, Ill.

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Cuming, Wm. F., 65 William St., Melbourne, Australia.
Dager, Herman J., 278 Jarvis St., Toronto, Canada.
Davis, Tenney L., 50 Mt. Vernon St., Somerville, Mass.
Emery, Arthur, Aurora, Ill.
Everhart, Edgar, College of Physicians and Surgeons, Atlanta, Ga.
Fleming, C. E., Box 13, Sandusky, Ohio.
Gooding, Charles 405 N. Willis Ave., Champaign, Ill.
Gross, Walter, 56 Caspian St., Elizabeth, N. J.
Guinzburg, Roland H., Du Bois, Penna.
Hanley, Henry B., 41 Whittier Ave., Providence, R. I.
Harris, J. E., Ann Arbor, Mich.
Heyder, Richard, 35 Commercial St., West Lynn, Mass.
Hoblitzell, Bruce, 7th and Ormsby Sts., Louisville, Ky.
Hunsicker, Thomas J., 501 Cumberland St., Lebanon, Penna.
Jennings, Maurice E., 9 W. Merrill St., Indianapolis, Ind.
Keck, J. H., Bloomington, Ind.
Kramer, Adolph S., 270 Broome St., New York City.
Kuh, Wm. H., 4404 Ellis Ave., Chicago, Ill.
Laib, Walter, 3112 Montgomery Ave., Philadelphia, Pa.
Leech, Paul N., 131 East High St., Oxford, Ohio.
MacLaren, J. B., 325 So Leavitt St., Chicago, Ill.
Marsh, Clarence W., cr. Development & Funding Co., New York City.
McBurney, Ralph, 612 Duncan St., Stillwater, Okla.
McCausland, H. S., 4879 E. Ravenswood Park, Chicago, Ill.
McGuigan, Hugh, 2431 Dearborn St., Chicago, Ill.
McMillan, S. A., College Station, Texas.
Missbach, Edmund C., Boise Chemical Institute, Boise, Idaho.
Moore, J. C., Franklin, Ind.
Moore, Landon C., 209½ Lane St., Dallas, Texas.
Overman, O. R., Windfall Ind.
Phillips G. C., 10 High St., Auburn, Maine.
Pomerantz, H. M., Cement, Solano Co., Calif.
Pratt, Nathaniel P., Atlanta, Georgia.
Rice, Ward J., Roachdale, Ind.
Robinson, John T., Columbia Falls, Mont.
Rood, Ellwood, D., 1320 Massachusetts Ave., Lawrence, Kans.
Rudy, Wm. D., 411 Walnut St., Philadelphia, Penna.
Skidgell, Floyd M., High Bridge, N. J.
Smythe, P. H., Mt. Healthy, Hamilton Co., Ohio.
Snyder, Seward, 213 North Washington St., Bloomington, Ind.
Spohrer, F. O., 102 S. 6th St., Columbia, Mo.
Stephenson, E. A., 5651 Drexel Ave., Chicago, Ill.
Stewart, Elmer, 1812 Lamont St., Washington, D. C.
Teeter, Arthur L., Monticello, Ind.
Thom, Wm. H., 410 Dovercourt Road, Toronto, Canada.
Tobitt, Miss Edith, Public Library, Omaha, Nebr.
Wheeler, Thorne L., Chatham, N. Y.
Williams, R. H., 808 Illinois St., Urbana, Ill.
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MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

PHILADELPHIA SECTION.

The regular meeting was held in the lecture room of the Chemical Laboratory of Swarthmore College, Swarthmore, Pa., on June 15th, at 8.30 P.M. The program consisted of an address on "The Secondary Metals," by Dr. Charles Baskerville, Professor of Chemistry, College of the City of New York. The lecture was illustrated by numerous charts, specimens of alloys, rare metals and minerals. A tube containing neon, through which the electric spark was passed, was exhibited and attracted great attention.

C. S. BRINTON, *Secretary*

UNIVERSITY OF MISSOURI SECTION.

At the last meeting of the Section the following officers were elected for the ensuing year: *President*, C. R. Moulton; *Vice-Pres.*, W. G. Brown; *Secretary*, L. D. Haigh; *Treasurer*, L. S. Palmer; *Councilor*, S. Calvert.

E. E. MORLAN, *Retiring Secretary.*

MILWAUKEE SECTION.

The annual meeting was held on June 25th, at Blatz Park. The following officers were elected for the ensuing year: *Chairman*, Frank S. Low; *Vice-Chairman*, Clarr H. Hall; *Secretary*, Ben. L. Salomon; *Treasurer*, Frank E. Layman; *Councilor*, George N. Prentiss. There was no formal program.

BEN L. SALOMON, *Secretary.*

DECEASED MEMBERS.

Dr. Julian W. Baird, June 26, 1911, Mass. College of Pharmacy, Boston, Mass.

Norman Ramsay, Mohammerah, Persian Gulf.

Dr. Harris E. Sawyer, Bureau of Chemistry, Washington, D. C.

ANNUAL INTERNATIONAL TABLES OF PHYSICAL AND CHEMICAL CONSTANTS.

At the International Congress of Applied Chemistry, held in London in 1909, an International Commission was appointed with power to undertake the publication of ANNUAL TABLES containing all constants and other numerical data which may be of interest in physics, in chemistry or in the technical applications of these sciences. The plans outlined by the Commission received the endorsement of the International Association of Academies, and the official recognition and financial support of many of the governments and learned academies of the world.

Owing to the immense volume of scientific and technical literature which is continually being produced, the difficulties in the way of ascer-

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taining whether any given measurement has been made or not are increasing year by year. Existing systems of indexing and abstracting offer only limited help, since a large number of measurements are made in the course of researches to which they are purely subsidiary, so that their existence cannot be inferred from the titles and sub-titles of the papers in which they are recorded. Also, tables which appear only at long intervals, such as those of Landolt and Börnstein, can of necessity cover only a small part of the ground and are never quite up to date. The ANNUAL TABLES should therefore fill a serious gap which has hitherto existed in the systematic indexing of scientific and technical results.

During the year 1910 all scientific publications which might contain material of value were systematically scrutinized by a large corps of abstractors. From the data thus obtained a volume of tables and bibliography is about to be published, covering the year 1910. The volume will form a valuable addition to the physical chemical tables which already exist and will, together with the succeeding annual volumes, prove a powerful aid to the work of the investigator both in pure and applied science. Each value given in the tables will be accompanied by the name of the author, by a reference to the original paper, and by an indication of the exact conditions under which the measurements were made.

It is expected that the publication of the tables will, after three or four years, become self-supporting. In the meantime, generous subscriptions have been made by governments, academies, scientific societies and individuals throughout the world; but further subscriptions must be obtained before the continued success of the project is assured. The General Secretary, Dr. Charles Marie, 98 Rue de Cherche-Midi, Paris, and the members of the International Commission serve without remuneration and the ANNUAL TABLES are to be published without financial profit.

Within a few weeks, subscriptions for the 1910 volume of the ANNUAL TABLES, *which is now in press, will be solicited. The price of the volume will probably be in the neighborhood of $5.00 or $6.00. From the nature of the publication it is necessary that a generous response be made in the form of a large number of subscriptions in all the scientific centers of the world.*

Information concerning the table or the work of the International Committee will be gladly furnished by the undersigned American members of the Committee.

G. N. LEWIS,
Massachusetts Institute of Technology, Boston, Mass.
G. F. HULL,
Dartmouth College, Hanover, N. H.
J. STIEGLITZ,
The University of Chicago, Chicago, Ill.

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THE JOURNAL

OF THE

American Chemical Society

THE VISCOSITY AND FLUIDITY OF EMULSIONS, CRYSTALLIN LIQUIDS AND COLLOIDAL SOLUTIONS.

BY EUGENE C. BINGHAM AND GEORGE F. WHITE.

Received April 24, 1911.

[Eleventh Communication Bearing on this Subject.]

Introduction.

That viscosity and fluidity may be considered to be analogous to electrical resistance and conductance, respectively, has already been pointed out by one of us.[1] The well known formula of Poiseuille, for the flow of a liquid through a capillary tube, may be written

$$\frac{8l}{\pi r^4 t} \cdot V = \frac{p}{H},$$

where V is the rate of transpiration, p the pressure, and H the viscosity coefficient; or since the term $\frac{8l}{\pi r^4 t}$ may be made a constant and equal to one, we have

$$V = \frac{p}{H} \qquad (1)$$

which is the analog of Ohm's Law, $C = E/R$.

Let us now consider the series of conductors shown in section in Fig. 1. Suppose, for the moment, that the surface AC be maintained at a potential which is higher than the surface BD. The resistance to the flow of current between the sur-

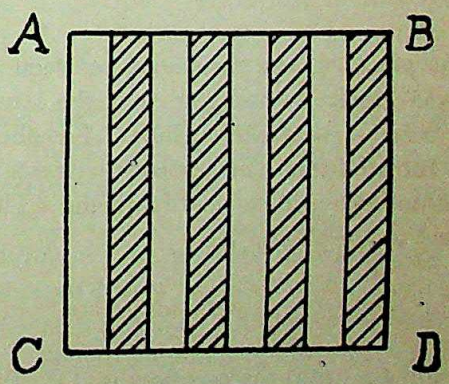

Fig. 1.

[1] *Am. Chem. J.*, 35, 195 (1906).

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faces will be the sum of the resistances of the different lamellae, thus

$$C = \frac{E}{r_1 + r_2 +},$$

or the resistance becomes

$$R = r_1 + r_2 + \ldots\ldots$$

Now if we imagin the lamellae to be capable of viscous flow and that the surface AB is subjected to a shearing force toward the right, it is evident that the resistance to flow will be the sum of the separate resistances, thus:

$$V = \frac{p}{\eta_1 + \eta_2 + \ldots}$$

or

$$H = \eta_1 + \eta_2 + \ldots \qquad (2)$$

We conclude, therefore, that *when viscous fluids are arranged in series, their viscosities are additive.*

If the surface CD is maintained at a constant potential difference above AB, the current will be the sum of the currents flowing through the separate conductors, thus:

$$C_1 = \frac{E}{r_1}$$

$$C_2 = \frac{E}{r_2}$$

and the total current is

$$C = C_1 + C_2 + \ldots = \frac{E}{r_1} + \frac{E}{r_2} + \ldots$$

$$= E\left(\frac{1}{r_1} + \frac{1}{r_2} + \ldots\right)$$

or

$$\frac{1}{R'} = \frac{1}{r_1} + \frac{1}{r_2} + \ldots,$$

where R' is the resistance between AB and CD.

If again we imagine that the lamellae of Fig. 1 are capable of viscous flow and that the surface CA is sheared upward with respect to the surface DB, then the resulting viscous flow will be found by adding together those for each separate lamella. Thus:

$$V_1 = \frac{p}{\eta_1}$$

$$V_2 = \frac{p}{\eta_2}$$

and the total viscous flow is

$$V = V_1 + V_2 + \ldots = p\left(\frac{1}{\eta_1} + \frac{1}{\eta_2} + \ldots\right)$$

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$$\frac{1}{H'} = \frac{1}{\eta_1} + \frac{1}{\eta_2} + \ldots$$

or since ϕ' is the reciprocal of H',

$$\phi' = \varphi_1 + \varphi_2 + \ldots \qquad (3)$$

When viscous liquids are arranged in parallel, their fluidities are additive.

The analogy is so nearly perfect that it is necessary to guard against one point of difference. In electrical flow, the conductors themselves remain stationary, while in viscous flow the substances themselves flow. Thus if we combine the two schemes referred to above, we will get a checkerboard arrangement of conductors for which the resultant resistance is intermediate between those of the two simpler patterns. Thus one might be led to suppose that in mixtures of liquids, the viscosity would always be intermediate between that given by the assumption that fluidities are additive and that given by the assumption that viscosities are additive. This might lead to serious error, for if in Fig. 1 the surface AB is sheared to the right in respect to the surface CD, the individual lamellae will tend to become inclined toward the right and very much elongated, and thus may come to assume the aspect depicted in Fig. 2. Thus although at the beginning the viscosities were strictly

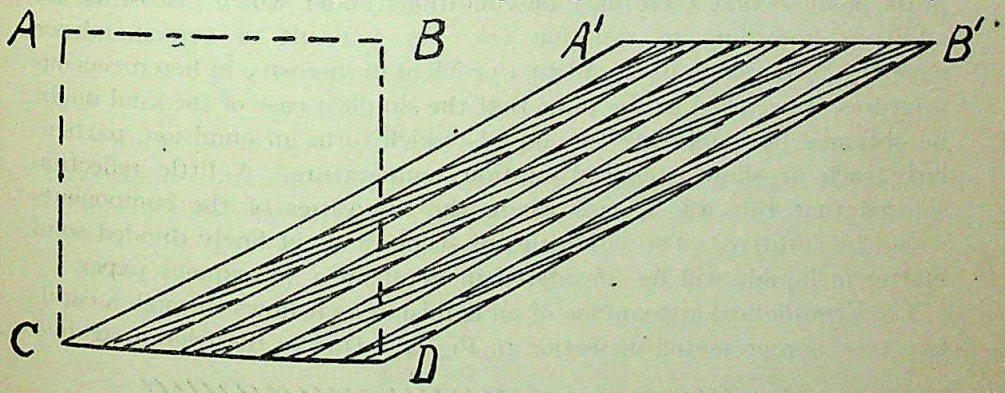

Fig. 2.

additive, as the viscous flow progresses, the conditions change more and more until the *fluidities* are additive. In miscible liquids, the condition that viscosities are additive would therefore appear to be fleeting, disappearing when the liquids are fully mixed. If the substances are immiscible, cohesion may prevent the elongation of the lamellae, in which case the viscosities may be additive as discussed below.

The stream lines around the openings of a capillary tube may be readily observed in the case of emulsions. They are shown in Fig. 3. It is seen that after flowing through the capillary, the liquid continues on for a considerable distance before its velocity is checked, thus apparently prolonging the capillary in this direction. As the liquid flows into the

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capillary, no such action is noticed. In other words, the liquid is drawn from a hemisphere around the opening, the result being that any portion of liquid, *A* in the figure, near the entrance of the capillary, considered as a sphere, suffers great elongation in passing into the capillary. The work of Osborne Reynolds, using colored liquids, should be mentioned as confirming this view. Hence we believe that *the conditions in homogeneous mixtures are always such that the fluidities are additive.* Dr. B. B. Turner has suggested to one of us the possibility of investigating this point on the basis of the kinetic theory. It is greatly hoped that this may be done.

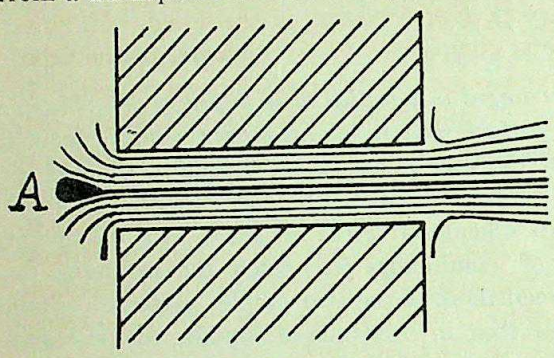

Fig. 3.

From the analogy between viscosity and electrical resistance, it appears possible that there may be conditions under which viscosities are additive, according to equation (2). As a result of correspondence with Dr. A. H. Sabin in regard to a problem in viscosity in heterogeneous mixtures, it occurred to one of us that the simplest case of the kind might be obtained by employing two liquids which form an emulsion, particularly such as show a critical-solution temperature. A little reflection showed that this was a case where the viscosities of the components would be additive. The viscosities of suspensions of finely divided solid matter in liquids will be considered in detail in a subsequent paper.

The hypothetical appearance of an emulsion as it flows through a capillary tube is represented in section in Fig. 4. Due to the friction against

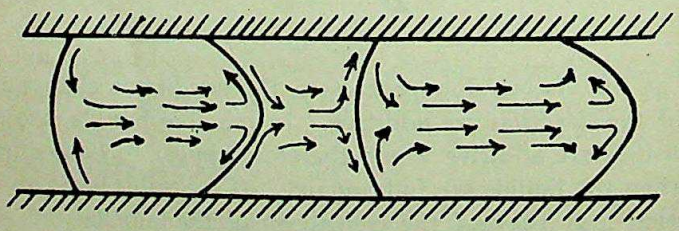

Fig. 4.

the walls, the front end of each drop tends to become abnormally convex and the rear end concave. It is to be specially noted that when the drops are small in diameter as compared with the diameter of the tube and yet large enough to occupy the whole cross-section of the tube, the

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motion of the liquid is by no means entirely linear, being transverse as well as longitudinal as indicated by the arrows. The effect of this transverse motion is to increase the apparent viscosity of the liquid. If, however, the drops are very large in comparison to the diameter of the tube, the importance of this transverse motion may be diminished to zero. It is self-evident from what has been said above that *if the drops of an emulsion are large enough to fill the cross-section of the tube, the viscosity, as measured by the method of Poiseuille, will be at least as great as the sum of the component viscosities.* It may be greater due to transverse motion. In the case of miscible liquids where the mixing is excessively imperfect, the resultant viscosity may also approach the sum of the component viscosities but it can never exceed it, because there can then be no transverse motion under the conditions for linear flow.

For liquids of limited solubility, it follows that above the critical-solution temperature, the fluidity of the homogeneous solution will be the sum of the component fluidities; but below the critical-solution temperature, the fluidities are no longer additive, but the viscosities may be. It remains now to determine whether the resulting fluidity will be uniformly greater or less when the viscosities are additive than it is when the fluidities are additive. We start from the equations representing these two assumptions:

$$H = a\eta_1 + b\eta_2 \qquad (2')$$

and

$$\Phi' = a\varphi_1 + b\varphi_2, \qquad (3')$$

where a and b represent the percentages of each of the components, assuming that only two are present. Since Φ is the reciprocal of H,

$$\frac{1}{\Phi} = \frac{a}{\varphi_1} + \frac{b}{\varphi_2}$$

or

$$\Phi = \frac{\varphi_1\varphi_2}{a\varphi_2 + b\varphi_1}.$$

When $a = 0$ or 1 and $b = 1$ or 0, Φ' must be equal to Φ. For all other values of a and b, we propose to prove that Φ' must always be greater than, equal to, or less than Φ. Multiplying equation (3)′ by unity, we have

$$\Phi' = \frac{(a\varphi_1 + b\varphi_2)(a\varphi_2 + b\varphi_1)}{a\varphi_2 + b\varphi_1}$$

$$= \frac{(a^2 + b^2)\varphi_1\varphi_2 + ab(\varphi_1^2 + \varphi_2^2)}{a\varphi_2 + b\varphi_1} \gtreqless \frac{\varphi_1\varphi_2}{a\varphi_2 + b\varphi_1}.$$

Since $b = a - 1$,

$$2a(a - 1)\varphi_1\varphi_2 + a(1 - a)(\varphi_1^2 + \varphi_2^2) \gtreqless 0.$$

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Discarding the known roots, $a = 0$ and $a = 1$, we obtain

$$\varphi_1^2 - 2\varphi_1\varphi_2 + \varphi_2^2 \gtreqless 0,$$

which is a perfect square and therefore must be positive, hence Φ' must always be greater than Φ. *Thus in every emulsion, the fluidity must be less than would be the case if the components formed a perfectly homogeneous solution.*

Historical.

When the literature of the subject was investigated, much evidence was found to support the above conclusion, but it was also found that several independent theories had been proposed to account for the facts.

Ostwald and Stebutt[1] observed an abnormally large viscosity in mixtures of isobutyric acid and water in the neighborhood of the critical-solution temperature. This was attributed to the fact that at the critical-solution temperature the surface energy becomes zero.

Friedländer[2] undertook to investigate the phenomena around the critical-solution temperature in an intensive manner. He found a very marked increase in the viscosity as the solution was cooled to temperatures where the opalescence became evident and the critical-solution temperature approached. He observed the opalescence with great care. His investigation was extended to include phenol and water, and the ternary mixture of benzene, acetic acid, and water. Similar relations were found in all proving that the phenomena are quite general. He concluded that the temperature coefficient of viscosity was greatest at the temperature where the opalescence and the tendency to foam were greatest. He says: "Der Trübungsgrad und temperaturkoefficient der inneren Reibung zeigen eine schr starke Zunahme in kritischen Gebiete und stehen mit einander in eineminnigen Zusammenhange." Friedländer also observed that the expansion coefficient and the coefficient of electrical conductivity and the refractive index remained normal. He believed that it was necessary to go farther than had Ostwald and that a definit radius of curvature of the separating surfaces must belong to each temperature, otherwise the degree of opalescence could not be definitly determined. He therefore attributed the increase in viscosity to the formation of drops, but he was puzzled by the fact that when a solution of rosin in alcohol is poured into a large quantity of water, a highly opalescent liquid is obtained which has, nevertheless, practically the same viscosity as pure water. This theory of Friedländer is apparently an outgrowth of the theory of "halbbegrenzte Tropfen" of Lehmann.[3] Friedländer discussed the electrical theory of Hardy[4] that an increase of work

[1] *Lehrb. der. allgem. Chem.*, 2 Aufl. 2^2, 684, etc.
[2] *Z. physik. Chem.*, 38, 385 (1901).
[3] *Molecularphysik.*, p. 270 (1888).
[4] *Z. physik. Chem.*, 33, 398 (1900).

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would be required to move the particles of a liquid among charged particles, so that if the "drops" were charged an increase in viscosity might result. He found by experiment that an electrical field was without noticeable effect upon an opalescent liquid. The values of viscosity given by Friedländer are not in absolute units.

Scarpa[1] made a study of the viscosity of solutions of phenol and water. His results are expressed in absolute units. For a given temperature he plotted the viscosities for different concentrations. The curves showed a point of inflection which was most marked at the critical-solution temperature. He tried to explain the irregularities on the assumption that hydrates were formed. He does not refer to the work of Friedländer.

Rothmund[2] started from Friedländer's work to make a study of the opalescence at the critical temperature. He measured the viscosities of butyric and isobutyric acid solutions in water, noting particularly the effect of the addition of various substances, both electrolytes and non-electrolytes, upon the opalescence. Rothmund objected to the hypothesis of Friedländer in that, according to the well known formula of Lord Kelvin, small drops are less stable than large ones, so that the small ones must disappear. Furthermore, he remarked upon the entirely analogous opalescence which is observed with a single substance at its critical temperature. Rothmund therefore called to his aid Donnan's hypothesis that when drops are very small their surface tension is very different from that of the liquid in bulk and is a function of the radius of curvature. Since at the critical temperature the surface tension is normally zero, it was thought that the small drops might thus exist in a state of stable equilibrium in the neighborhood of the critical-solution temperature. As the temperature was raised the opalescence would become less and less, due to the solution of the drops. Rothmund found that the addition of naphthalene to his solutions greatly increased the opalescence, while the addition of grape sugar decreased it very greatly, although the effect of these additions upon the viscosity was negligible. Rothmund reasoned that the refractive index of butyric acid is greater than that of water and sugar and electrolytes raise the refractive index of water, hence they make the presence of small drops less evident. Naphthalene does not dissolve in water but does dissolve in the butyric acid, raising its refractive index, and therefore makes the opalescence more apparent.

Von Smoluchowski[3] regards Rothmund's hypothesis as superfluous, believing that the kinetic theory is sufficient to explain the opalescence. According to him, differences in molecular motion, local differences in

[1] *Cimento* [5] 5, 117 (1903) and *J. chim. phys.*, 2, 447 (1904).
[2] *Z. physik. Chem.*, 63, 54 (1908).
[3] Drude's *Ann.*, 25, 205 (1903).

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density, and therefore differences in surface tension cause the critical temperature to be not entirely definit, resulting in a rough surface which must remain of smaller thickness than a wave length of light, since greater thicknesses would not reflect light. The inequalities in the density become a maximum at the critical temperature.

Bose and his co-workers[1] have also verified the earlier observations that abnormally large viscosities are obtained at the critical-solution temperature. Bose regards this as being due to the rolling of drops of liquid along the capillary. They did a considerable amount of work to prove that "crystallin" or "anisotropic" liquids are similar to the emulsions here discussed. Bose proved that these liquids have abnormal viscosities near the clarifying point and they also possess marked opalescence. They started from the work of Vorländer and Gähren,[2] who found that a crystallin liquid might result from the mixing of two liquids neither of which was itself "crystallin" in the pure condition. The mixture therefore resembles an emulsion. Bose regards all "crystallin" liquids as emulsions of very long life, *i. e.*, they settle out with extreme slowness; and he proposes an extension of the kinetic theory to account for them. According to van der Waals, the molecules are to be regarded as spheres. However, the molecules of the substances known to form "crystallin" liquids do not approximate to a spherical form but consist of two or more benzene rings united in such a way as to make a rather elongated compound. Hence Bose thinks that they might be better represented by ellipsoids of revolution. As the temperature is lowered, these molecules naturally arrange themselves with their long axes in parallel planes. As the molecules thus unite to form "swarms," the viscosity is increased. This ordered arrangement also causes the liquids to show double refraction.

It was shown that quite often the viscosity *increases* rapidly as the temperature is raised at the clarifying point, but there is also then an increase in density.

It occurred to Bose, Willers, and Rauert[3] that the orderly "swarm" arrangement might be destroyed by measuring the viscosity under conditions for turbulent flow. It was shown by them, in fact, that the abnormalities at the critical-solution temperature do decrease as the transpiration velocity is increased. But these results are not very conclusive, since the conditions of turbulent flow are themselves not very thoroughly understood. Pure liquids were studied under conditions of turbulent flow and it was found that there is not a complete parallelism be-

[1] *Physik. Ztschr.*, 8, 313 (1907); 8, 347 (1907); 9, 769 (1908); 9, 707 (1908); 10, 32 (1909); 10, 230 (1909); 10, 406 (1909). *Z. Elektrochem.*, 8, 449 (1907).

[2] *Ber.*, 40, 1966 (1907).

[3] *Physik. Z.*, 10, 406 (1909).

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tween the viscosities measured by the two methods. In fact, there are several cases where one substance has a higher viscosity than another substance under the conditions for linear flow, but a lower viscosity under the conditions for turbulent flow. For this no explanation has been given. Schenck, Eichwald, Bühne, and Dunkenscheid have worked in this field, but we have not had access to their work.

Bose measured the viscosities of suspensions of finely divided quartz particles in bromoform and water and found, as did Friedländer, that the suspended substance affected the viscosity of the solvent but little. There is a paucity of literature on this subject.

Several investigators have worked on the viscosity of colloidal solutions. Now if the "foam-cell" or some similar theory of colloidal solutions is correct, that the solidification of the solution is accompanied by the separation into two phases, then the peculiarities in the viscosities of colloidal solutions may possibly be explained by the considerations which are the object of study in this paper.

Griffiths[1] studied the viscosity and electrical resistance of gelatin solutions. He found that one part of gelatin and five parts of sodium chloride dissolved in ten parts of water at 20° gave an electrical resistance which was always *less* than that of a solution free from gelatin. On the other hand the viscosity continually increased. So far as his experiments went, they indicated no connection at all between the viscosity of the mixture and the internal friction opposing the movements of the ions.

Levites[2] studied the rates of gelatinization when various substances were added to the solution of gelatin and other colloids. He found that the salts of monobasic acids lessen the velocity of gelatinization, while salts of the di- and tribasic acids increase this velocity. He tried to relate this to viscosity, but he found that at the higher temperatures the viscosity is independent of the amount of colloid and is dependent upon the amount of dissolved substance only.

Garrett[3] made an interesting study of several colloidal solutions and measured their viscosities by both the transpiration method and the method of an oscillating disk. In a homogeneous liquid the logarithmic decrements of the amplitude of vibration of an oscillating disk are constant, but in solutions of gelatin, silicic acid, and albumen they increase. Garrett explains this on the assumption that the "cells" of the highly viscous phase become attached to the disk. It is in harmony with this explanation that when the disk is thoroughly cleansed and reintroduced

[1] *Proc. Manchester Lit. and Phil. Soc.*, 41, 9 (1896).
[2] *J. Russ. Phys. Chem.*, 35, (1903).
[3] *Phil. Mag.*, [6] 6, 374 (1903).

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into the liquid, the original value of the logarithmic decrement is restored. Moreover, an exceptionally large vibration dislodges some of the cells, thereby causing an increased logarithmic decrement for the succeeding vibrations.

Below a certain temperature a richly colloidal solution separates out slowly as a "liquid precipitate" with a constantly increasing viscosity in whatever way the viscosity may be measured. On continued boiling, the "cell-walls" are destroyed and a gelatin solution then resembles a homogeneous liquid. Other interesting and suggestive relations may be found in the original paper.

Müller[1] compared the "gold numbers" of various colloidal solutions with their fluidities and showed that there is a relation between them as shown by the following table:

Substance.	Fluidity as compared with water at 15°.	Gold number.
Gelatin	0.693	0.005–0.01
Casein	0.824	0.01
Glue	0.924	0.15–0.4
Tragacanth	0.933	About 2
Dextrin	0.973	6–20
Potato starch	0.980	25
Cane sugar	0.998	∞

The gold number is defined "as the number of milligrams of colloid which are just sufficient to prevent the change to violet of ten cubic centimeters of bright red colloidal gold solution by the addition of one cubic centimeter of a ten per cent. solution of sodium chloride."

The ions of the sodium chloride serve as nucleating centers. It now becomes clear why an excessively large addition of cane sugar is required to delay the nucleation appreciably, since the fluidity of the solution differs so little from that of water. On the other hand, the gelatin solution has a much lower fluidity than water, hence the nucleation is considerably retarded by a small addition.

Von Schroeder[2] used the viscosity method for studying the behavior of solutions of gelatin. He found that the viscosity of a given solution at a given temperature was not a constant but depended largely upon the past history of the solution. He differentiated two sets of phenomena, as follows: 1. An irreversible saponification, which is greatly increased as the temperature is raised, and is a logarithmic function of the time. 2. A reversible "gel-sol" transformation. The gelatinization takes place at low temperatures, causing the increase in viscosity, but an indefinit time is required for equilibrium to be established at a given temperature.

[1] *Ber.*, 37, 11 (1904).
[2] *Z. physik. Chem.*, 45, 75 (1903).

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The effects of different acids, bases, and salts were investigated and found to be quite diversified.

Woudstra[1] worked with colloidal silver solutions and showed that the viscosity decreases with the time and on the addition of electrolytes, but increases with the concentration of the colloid. Both of the first effects are due to coagulation. Woudstra believes that this is due to the lack of that coherence in the surfaces which come into contact, which is present in the gelatin solutions.

Experimental.

Thorpe and Rodger[2] and others have already shown that the horizontal tube method of Poiseuille may be used for measuring viscosities with exceedingly satisfactory results. This is not altogether true of the Ostwald viscosimeter, which is the form that is perhaps most commonly used. On the other hand, the latter type is exceedingly simple to set up and use, while the former type requires a large amount of preliminary work, and the measurements themselves are much more complicated. It therefore seemed worth while to spend some effort in the attempt to increase the accuracy of the one method, so that the present great disparity between the two methods might be eliminated, or to so simplify the other method that it might be adapted for general use.

Our object at the time was to study intensively some solutions of non-electrolytes in water, which have been shown in a previous paper[3] to be abnormal in that they do not give linear fluidity curves. This so-called "abnormality" is doubtless due to the formation of hydrates; and since in the study of viscosity and fluidity, it has already been shown[4] by one of us that the molecular condition within a liquid may be learned by means of fluidity data, it was hoped that some light might be thus thrown upon the question of hydrates in solution. However, before this problem was finished, the problem arose which is the subject of discussion in this paper. We have therefore used our apparatus for its solution, but we will delay giving the details in regard to our apparatus until a succeeding paper. Suffice it for the present to say that the apparatus consisted of a horizontal capillary of known length and cross section, which was connected to two vertical arms by means of carefully ground glass joints. The vertical arms were so arranged as to allow a perfectly definit amount of liquid to flow through the capillary under conditions which practically eliminated the effect of hydrostatic pressure. The vertical arms were connected to an air reservoir under pressure, the pressure being measured

[2] *Z. physik. Chem.*, 63, 619 (1908).
[3] *Phil. Trans.*, 185A, 397 (1894).
[1] *Amer. Chem. J.*, 35, 195 (1906).
[2] *Z. physik. Chem.*, 66, 1 (1909).

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by a water manometer. The apparatus was carefully tested and found to give absolute viscosities which agree very well with the values of Poiseuille, Slotte, Thorpe and Rodger, and others.

For the study of emulsions, the apparatus proved rather tedious to manipulate on account of the difficulty of getting satisfactory mixture of the solutions after they had once separated out. This was best accomplished by blowing air through the solutions, the precaution being taken to have the aqueous pressure such that the evaporation from the emulsion would be negligible. That the results were satisfactory was indicated by the duplication of results.

In the choice of mixtures one is restricted. Isobutyric acid and phenol both give critical solutions with water which are readily reached. Consequently these mixtures have already been studied repeatedly. Only once have the absolute viscosities of such mixtures been obtained. Moreover, it is especially desirable that the same pairs of substances should be studied, using capillaries of different dimensions, or even using different methods. Consequently phenol and water were chosen for study. The water was redistilled from chromic acid and barium hydroxide with particular care to eliminate all dust. The phenol was fractionated by distillation and crystallization. It boiled at 182.4° under 763 mm. pressure. At the close of the investigation it melted at 38°, indicating the presence of a small amount of impurity, but a trace of water could not affect the viscosity of our emulsions.

It seemed more likely that any relation would be apparent when the solutions were made up on the basis of molecular per cent. Thus a ten per cent. phenol solution is a solution containing 10 × 94.05 grams of phenol and 90 × 18.02 grams of water. The specific gravities were determined by means of an Ostwald pycnometer.

The following tables show the results obtained:

TABLE I.—THE FLUIDITY OF PURE PHENOL.

Temp.	Fluidity. Left limb.	Fluidity. Right limb.	Temp.	Fluidity. Left limb.	Fluidity. Right limb.
33.96°	16.64	...	60.00°	39.02	39.01
35.98	...	17.93	65.00	44.44	44.45
36.60	18.36	...	70.00	50.14	50.04
40.00	...	20.82	75.00	56.25	56.16
45.00	25.02	...	79.97	62.52	62.65
50.00	29.23	29.24	85.03	69.41	69.64
55.00	34.01	34.05	90.15	...	76.70

The values of the fluidity of pure phenol were plotted to a large scale, and the values for every five degrees were read off. These are given in Table II:

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TABLE II.—THE FLUIDITY OF PURE PHENOL FOR EVERY 5°.

Temp.	Fluidity.	Temp.	Fluidity.
35.00°	16.60	65.00°	44.46
40.00	20.82	70.00	50.06
45.00	25.00	75.00	56.18
50.00	29.24	80.00	62.64
55.00	34.03	85.00	69.48
60.00	39.03	90.00	76.56

TABLE III.—THE FLUIDITY OF 20 PER CENT. PHENOL IN WATER.

Temp.	Fluidity. Left limb.	Fluidity. Right limb.	
59.00°	76.31	...	
64.00	82.94	81.78	
65.00	85.32	84.43	Cooled quickly from above critical-sol. temp.
66.00	87.35	86.36	Critical-solution temperature.
67.00	89.53	88.91	Slight opalescence.
68.00	91.34	89.99	
70.00	95.40	95.60	
73.20	102.3	101.8	
75.00	104.7	104.7	
79.90	115.1	115.3	
85.00	126.6	126.1	
90.00	136.8	136.2	
95.00	147.3	146.8	

TABLE IV.—THE FLUIDITY OF 10 PER CENT. PHENOL IN WATER.

Temp.	Fluidity. Left limb.	Fluidity. Right limb.	
26.00°	32.04	...	
70.00	98.91	98.87	
73.00	103.9	103.2	
73.20	106.6	106.5	Critical-solution temperature.
75.00	118.0	118.3	Opalescence. Appearance as indicated in Fig. 6.
80.00	136.5	135.6	
85.00	...	150.7	
90.00	164.8	165.0	
95.00	179.3	179.3	

TABLE V.—THE FLUIDITY OF 5 PER CENT. PHENOL IN WATER.

Temp.	Fluidity. Left limb.	Fluidity. Right limb.	
71.50°	164.4	160.5	
72.50	165.6	165.1	Critical-solution temperature.
73.00	167.5	167.6	Liquid perfectly clear with no opalescence.
75.00	174.5	174.6	
80.00	190.1	191.7	
85.00	204.5	206.4	
90.00	221.6	222.7	
95.00	238.7	238.5	

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In all of the mixtures it is to be observed that the fluidity increases with the temperature very rapidly in the neighborhood of the critical-solution temperature. This is shown graphically in Fig. 5.

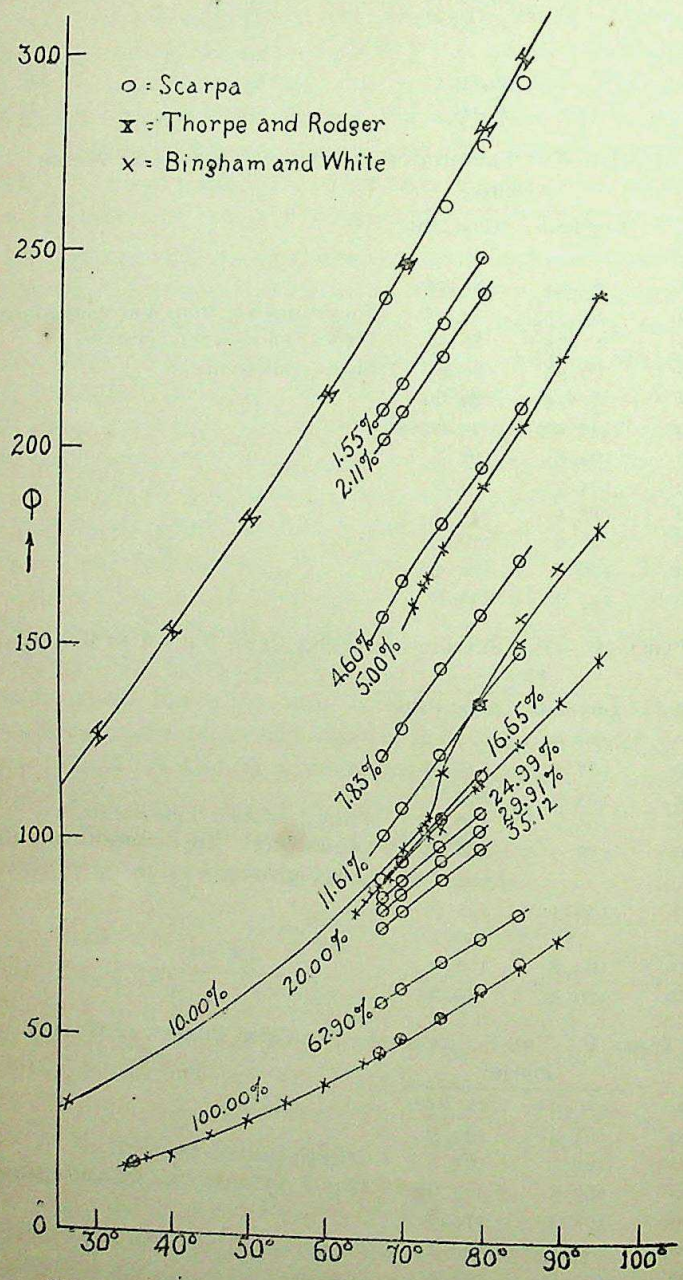

Fig. 5.—The fluidities of phenol and water mixtures.

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TABLE VI.—THE FLUIDITIES OF PHENOL AND WATER MIXTURES AS CALCULATED FROM THE DATA OF SCARPA.

Concentrations in molecular per cent.	Temperatures.				
	67.5°.	70.0°.	75.0°.	80.0°.	85.0°.
0.00	238.1	246.9	261.1	276.24	292.4
1.55	209.6	216.4	232.0	248.1	...
2.11	202.0	209.2	223.2	239.2	...
4.60	157.2	166.1	181.1	195.32	210.1
7.83	122.0	129.4	144.9	158.7	171.8
11.61	101.8	108.9	123.0	135.9	148.8
16.65	90.91	96.16	106.38	117.92	...
24.99	86.21	90.66	99.01	107.99	...
29.91	83.20	87.26	96.16	103.73	112.11
35.12	78.74	83.12	90.74	99.50	...
62.90	60.10	63.37	70.92	76.92	83.89
100.00	47.39	50.35	56.43	63.65	70.62

Discussion of Results.

It is to be noticed that our data for pure phenol agree satisfactorily with that of Scarpa at the low temperatures. At high temperatures the deviation is far too great, being nearly two per cent. at 85°. Scarpa's data for pure water also differs from the values of other observers at high temperatures, the value at 85° being 2 per cent. lower than the value given by Thorpe and Rodger. When we consider the much greater difficulties in introducing the mixtures into the viscosimeter and keeping the liquids mixed, it is not surprising that the agreement for them is even less satisfactory. We have studied a few mixtures at many temperatures. Scarpa studied many mixtures at a few temperatures. Both investigations agree in showing that there is at least a tendency for the fluidity to fall off abnormally as the temperature is lowered to the critical-solution temperature. Not all of the mixtures show this falling off to the same extent nor does the same mixture appear to give the same curve when measured in different forms of apparatus. Thus our 10 per cent. mixture and Scarpa's 11.61 per cent. mixture give entirely different curves. Furthermore, our own data show that, although our measurements were made with great care, the values of the fluidity near the critical-solution temperature do not always agree with each other. We believe that the explanation of these distressing differences is partly that, in an emulsion, the fluidity is dependent upon the size of the drops and the dimensions of the apparatus, the viscosity being greatest when the drops are large in comparison with the cross-section of the capillary. That the fall in fluidity at the critical-solution temperature cannot be due to lack of complete mixing can be proved in the case of our own measurements by the fact that the heavier liquid was also the more viscous. If this settled out, it would be driven through the capillary before the measurement began. The remaining liquid which would be

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used for the measurement would therefore possess too great a fluidity. Hence the drop in the fluidity at the critical-solution temperature must be a real effect. Furthermore, we may point out that the same irregularity of the results is shown by the work of Friedländer, for some of his curves cross each other. To test still further the effects of better mixing than we were able to get, we measured the viscosity of our 5 per cent. emulsion from 25° to 75° in a modified Ostwald viscosimeter. The drop in fluidity at the critical-solution temperature was quite apparent.

Lastly, we again made up a 20 per cent. solution of phenol, which we had found to give results not agreeing with those of Scarpa and measured its fluidity to see whether an error had crept into our work at some step. The mixture contained 8.221 g. of phenol and 6.302 g. of water. The fluidities measured at 80° and 85° were as follows:

	Fluidity.	
Temp.	Left limb.	Right limb.
80.00°	115.56	115.53
85.00	125.70	125.69

Our earlier measurements for the same temperatures were:

80.00°	114.62	115.55
85.00	126.62	126.09

The agreement is sufficiently satisfactory, hence no further measurements were made with this mixture.

Let us now recapitulate the explanations which have been offered to explain this drop in fluidity, as follows:

1. The electrical theory of Hardy.
2. The surface energy theory proposed by Ostwald and modified by Friedländer and Rothmund.
3. The theory of hydrates of Scarpa.
4. The rolling drops of Bose.
5. With the above should be grouped the attempted explanation by von Smoluchowski of the opalescence of liquids, as due to differences in density, for the opalescence of liquids and the decrease in fluidity seem to be intimately associated.
6. To these we add our own explanation on the basis of the theory of viscosity.

In regard to the first two, sufficient remark was made in the historical part of this paper. Scarpa's explanation by the assumption of hydrates seems unnatural, because it would be reasonable to suppose that the hydrates would be formed, if at all, as the phenol and water dissolved in each other and that this hydration would be connected with an increase of viscosity. On the contrary, we find the increased viscosity as the mixture separates out into two phases.

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Bose would explain the phenomenon on the basis of the transverse motions discussed in the first part of this paper. This loss of energy by transverse motions will decrease as the drops become larger and become zero as the liquids become completely separated out. Hence this is inadequate as a complete explanation although it may explain some of the irregularities in the measurements at the critical-solution temperature.

The difficulty with our own explanation seems to be to explain why the drop in fluidity begins before the critical-solution temperature is actually reached, *viz.*, in the opalescent condition of the liquid. It does not seem reasonable that discreet "drops" can exist several degrees above the critical-solution temperature, therefore the explanation of Rothmund for the fall in fluidity lacks probability. But all that is necessary is that there should be incomplete mixing in the liquid, and this is the basis also of the explanation of opalescence by von Smoluchowski. Near the critical temperature any slight changes in temperature have a maximum effect and while no drops may be formed nor the critical temperature reached in any part of the liquid, since the temperature of the liquid may be maintained at a temperature several degrees above the critical temperature, nevertheless the liquid may become poorly mixed. This conception may be made more definit as follows: At the critical-solution temperature the affinity of molecules of phenol for other molecules of phenol and of molecules of water for other molecules of water becomes equal to the affinity between the phenol and water. At temperatures even considerably above the critical-solution temperature, some of the phenol molecules and some of the water molecules must have velocities below the critical value. The result will be that the molecules of phenol will group themselves together, and if they reach sufficient size before being redissolved, the action of gravity will be appreciable in causing a separation of the liquids. The particles may be ultramicroscopic and not properly regarded as "drops," though perhaps not very different from the "halbbegrenzte Tropfen" of Lehmann. We do not think that it is necessary to go so far as von Smoluchowski in assuming that the critical-solution temperature is not entirely definit.

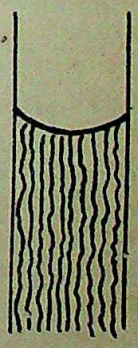
Fig. 6.

The simple way of regarding the phenomenon outlined above is borne out by the optical appearance of the liquid in the opalescent condition. We have observed that whenever the liquid was opalescent, if the liquid was observed by direct light, unequal refraction could be seen as suggested by Fig. 6. The partial separation of the liquid into parts of different densities explains at the same time both the opalescence and the increase in viscosity. It is only necessary for

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a liquid of a given density to fill the cross-section of the capillary at any time in order to make the viscosities additive and, as we have shown, the viscosity must then be greater than in a thoroughly mixed solution.

It is evident that this explanation is at once applicable to the increase in viscosity in crystalline or "anisotropic" liquids. It is only necessary that the "swarms" be of sufficient size in order that the viscosities of the components of the liquid shall be additive.

In colloidal solutions, the "foam-cell" theory is already based upon the assumptions which make the above explanation immediately applicable. As a gelatin solution sets, a "liquid precipitate" is formed which has a very high viscosity. The liquid filling the cells of this precipitate has a viscosity not very different from water. Since the viscosities are here additive, the viscosity of the mass is very high even though the electrical resistance is low. The ions evidently wander through the medium of low viscosity, in the interstices of the jelly.

It becomes evident why very opalescent suspensions, such as that tested by Friedländer, of rosin suspended in water, give viscosities which are not different from the viscosity of pure water. The particles in this case are so very small that they are incomparably smaller than the cross-section of the capillary, hence the fluidities are additive. The fluidity of rosin is certainly nearly zero, so that when it is present in small amounts it does not affect the fluidity of water appreciably. That the particles are indeed small is shown by the fact that such a suspension of rosin will not settle if left for many weeks. On the other hand, a little water added to a solution of rosin in alcohol will give an emulsion containing two liquid phases which behaves exactly like the emulsion of phenol and water. We believe that no explanation has been given for these phenomena heretofore.

The decrease in the viscosity of colloidal silver solutions on standing is explained by the gradual deposition of the silver as a very fine solid suspension which does not affect the viscosity appreciably, as in the case of small amounts of rosin in water, when the particles are small, the *fluidities* are additive, hence the solid silver particles do not exert much influence upon the viscosity until the particles become aggregated together.

In another paper, the fluidities of solid suspensions will be considered in detail. It will be shown that simple laws govern the relation of fluidity to concentration, which are in harmony with the above considerations. Moreover, when a suspension is coagulated by any means, as by the addition of a trace of electrolyte, there is a marked decrease in the fluidity.

We therefore conclude that when liquids are thoroughly mixed, their fluidities will be additive; but if the liquids form an emulsion, a crystallin liquid, a colloidal solution, or if the mixture is for any other reason

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incomplete, the fluidity of the mixture will be less than would be the case in a homogeneous solution. This conclusion can be deduced mathematically and it is verified experimentally. These experimental facts have been known for a long time and several theories have been proposed to account for them. We have indicated that some of these are not inconsistent with our explanation, though others are unnecessary if not untenable.

We wish to acknowledge indebtedness to Dr. R. E. Loving for suggestions in the preparation of this paper.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 197.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. IX. THE DROP WEIGHTS OF THE ASSOCIATED LIQUIDS, WATER, ETHYL ALCOHOL, METHYL ALCOHOL AND ACETIC ACID; AND THE SURFACE TENSIONS AND CAPILLARY CONSTANTS CALCULATED FROM THEM.

BY J. LIVINGSTON R. MORGAN AND A. McD. McAFEE.

Received June 2, 1911.

In the previous papers of this series the modified definition of normal molecular weight in the liquid state,[1] *viz.*, the finding of a calculated value of t_c in the relationship

$$w\left(\frac{M}{d}\right)^{\frac{2}{3}} = k_B\,(t_c - t - 6),$$

where k_B is found by a similar equation for benzene, using for t_c its observed critical temperature, 288.5°, has been applied to the drop weight results, on the Morgan drop weight apparatus, of forty-five (45) different liquids, with the result that all, with but four (4) exceptions, dimethylaniline, and the methyl, ethyl, and propyl formates, are found to be perfectly normal and non-associated, the value of t_c remaining constant, within reasonable limits, at the various temperatures of observation. Slight differences are to be expected here, of course, due to variations in the densities, unless these are also determined on the sample of liquid used.

In the cases of the four exceptions, as has already been pointed out, the dimethylaniline probably undergoes a rapid and permanent decomposition, which affected, in this work, the result at the higher temperature of observation, but not that at the lower; while there are indications that the formates undergo, with increased temperature, a decomposition, or change of some sort, which persists for several days after the liquid cools slowly to a lower temperature, but not when it cools rapidly. For the

[1] Morgan, THIS JOURNAL, 33, 648–649 (1911).

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present, then, these liquids must be considered as belonging in a class by themselves, the observed complications existing allowing them to be considered neither as typically non-associated, nor as typically associated.

The object of this paper is to present the results obtained with the new apparatus with the typical associated liquids, water, ethyl alcohol, methyl alcohol and acetic acid, where no complications of this sort exist. It is to be expected here that the calculated value of t_c will change with the temperature of observation, increasing with an increase in that, but in such a way that the change should not persist when the temperature is decreased either slowly or rapidly—in other words, the value of t_c from these typical liquids should under all conditions be a function of the temperature of observation, uninfluenced by that at which it was held previously.

The liquids used were all purified according to the methods advocated by previous workers on capillary rise, while the constant temperature bath, for temperatures from 0°–77°, was that described recently by Morgan.[1]

The drop weight results for benzene at 60.4°, from which the standard k_B of the tip was found, are given in Table I.[2]

TABLE I.—BENZENE; M = 78; t_c = 288.5°.

t.	Wt. vessel + 30 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
60.4	9.4232 9.4229	9.42305	8.7888 8.7888	8.7888	25.370

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	k_B.
60.4	0.83583	25.370	521.979	2.3502

From this value of k_B, 2.3502, using the equation

$$k_B = 0.4224 \times 2r$$

(see No. 8), we find that the diameter of this tip was 5.56 mm.

In order that this value of k_B might be checked, before using the tip for the new liquids, the drop weight at 60.3° of freshly distilled quinoline was determined, with the result given in Table II.

TABLE II.—QUINOLINE; M = 129.

t.	Wt. vessel + 30 drops.	Av.	Wt. vessel + vapor.	Wt. 1 drop. Mg.
60.3	9.9562 9.9560	9.9561	8.6487	43.580

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c from k_B = 2.3502.
60.3	1.0615	43.580	1069.3	521.3

[1] THIS JOURNAL, 33, 344–349 (1911).

[2] The same value of k_B was also found at other temperatures, the results for which need not be given.

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As Morgan also found, from the results of Morgan and Higgins (see No. 4), the same t_c, 521.3°, for quinoline, this value of k_B, as the standard of the tip, is to be regarded as satisfactory.

In Tables III–VI inclusive, are given the experimental values for water, ethyl alcohol, methyl alcohol and acetic acid, at various temperatures of observation. The temperatures here, at 30° and below, were read on a certified thermometer, divided into fiftieths of a degree, those above being observed on one reading in tenths, also certified. With water, at first, the same difficulty observed by Rayleigh[1] was encountered, *i. e.*, a decrease in the weight of the drop after taking down the apparatus and repeating the measurement. This difficulty, due to impurity on the tip, was readily avoided, however, by cleaning the tip just before each determination with a sulfuric and chromic acid mixture, and washing with alcohol, ether, and finally, water. In this way very good checks were easily obtainable.

TABLE III.—WATER.

t.	Weight vessel + 30 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.0	11.1770		....		
	11.1770	11.1770	9.4905	9.4905	84.325
	11.1770		9.4905		
1.8	11.1697	11.1695	9.4886	9.4886	84.045
	11.1693		9.4886		
4.0	11.1572	11.1572	9.4844	9.48445	83.638
	11.1572		9.4845		
6.0	11.1459	11.14625	9.4804	9.4804	83.293
	11.1466		9.4807		
	...		9.4801		
7.5	11.1387		....		
	11.1382		9.4781		
	11.1389	11.13852	9.4780	9.47798	83.027
	11.1385		9.4778		
	11.1383		9.4780		
	11.1385		....		
12.95	11.1088	11.10845	9.4678	9.4678	82.033
	11.1081		9.4678		
15.0	11.0973		....		
	11.0964	11.09686	9.4640	9.4640	81.643
	11.0969		9.4640		
17.0	11.0858		....		
	11.0862	11.08626	9.4605	9.46045	81.291
	11.0868		9.4604		
19.25	11.0740	11.0740	9.4556	9.4556	80.920
	11.0740		9.4556		
22.5	11.0555	11.05565	9.4495	9.4495	80.308
	11.0558		9.4495		

[1] *Phil. Mag.*, [5] 48, 324 (1899).

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TABLE III.—(*Continued*).

t	Wt. vessel + 30 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
25.3	11.0422 11.0429	11.04255	9.4464 9.4466	9.4465	79.803
27.81	11.0275 11.0281	11.0278	9.4409 9.4412	9.44105	79.338
30.0	11.0174 11.0176 11.0166	11.0172	9.4383 9.4385 9.4384	9.4384	78.940
36.46	10.9797 10.9804	10.98005	9.4252 9.4249	9.42505	77.750
40.0	10.9608 10.9608	10.9608	9.4195 9.4193	9.4194	77.070
45.0	10.9323 10.9315	10.9319	9.4105 9.4105	9.4105	76.070
55.0	10.8735 10.8737 10.8732	10.87346	.... 9.3921 9.3919	9.3920	74.073
60.0	10.8456 10.8456	10.8456	9.3825 9.3828	9.38265	73.148
70.0	10.7821 10.7819	10.7820	9.3604 9.3609	9.36065	71.068
77.0	10.7410 10.7410 10.7419	10.7413	.... 9.3487 9.3487	9.3487	69.630

TABLE IV.—ETHYL ALCOHOL.

t.	Wt. vessel + 30 drops.	Av.	Wt. vessel + 10 drops.	Av.	Wt. 1 drop. Mg.
0.0	9.3168 9.3168 9.3168	9.3168	8.7988 8.7988	8.7988	25.900
10.0	9.3969 9.3966	9.39675	8.8964 8.8968	8.8966	25.008
20.0	9.3702 9.3702	9.3702	8.8878 8.8878	8.8878	24.120
40.0	9.3197 9.3201 9.3200	9.31993	.... 8.8735 8.8733	8.8734	22.327
50.0	9.2955 9.2955	9.2955	8.8660 8.8661	8.86605	21.473
60.0	9.1663 9.1656 9.1660	9.16596	.... 8.7537 8.7539	8.7538	20.608
65.0	9.2613 9.2616	9.26145	8.8575 8.8574	8.85745	20.200
70.0	9.2506 9.2507	9.25065	8.8539 8.8543	8.8541	19.828

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TABLE V.—METHYL ALCOHOL.

t	Wt. vessel + 30 drops.	Av.	Wt. vessel + 10 drops.	Av.	Wt. 1 drop. Mg.
0.0	9.4379		8.9104		
	9.4383	9.4379	8.9100	8.91026	26.382
	9.4375		8.9104		
20.0	9.3819		....		
	9.3822	9.38223	8.8918	8.8917	24.527
	9.3826		8.8916		
30.0	9.3565	9.35665	8.8846	8.8840	23.603
	9.3568		8.8846		
40.0	9.3300	9.32975	8.8764	8.8765	22.663
	9.3295		8.8766		
50.0	9.3042		8.8694		
	9.3045	9.3045	8.8694	8.8694	21.755
	9.3048		8.8694		

TABLE VI.—ACETIC ACID.

t.	Wt. vessel + 39 drops.	Av.	Wt. vessel + 10 drops.	Av.	Wt. 1 drop. Mg.
20.0	9.5445		....		
	9.5438	9.54417	8.9464	8.9464	29.889
	9.5439		8.9464		
	9.5445		8.9464		
40.0	9.4820		8.9268		
	9.4824	9.48246	8.9270	8.9270	27.773
	9.4830		8.9272		
60.0	9.4239		....		
	9.4243	9.4242	8.9100	8.9100	25.710
	9.4244		8.9100		
70.0	9.3960	9.39625	8.9023	8.90225	24.700
	9.3965		8.9022		

Throughout in this work both ventilation tubes were connected to drying tubes, and pure dry air was bubbled through for some time before each determination, so that *all the results are for the liquids when saturated with air at the temperature of observation.*

Since these liquids, being associated, do not lead at all temperatures of observation to the same calculated value of t_c, it is necessary to find some means of transforming the above results of drop weight into surface tension in dynes per centimeter. In the previous papers, for this purpose, the ratio

$$w_t : \gamma_t :: k_B : K_B$$

has been used, the value of the constant of capillary rise, K_B, being found from the benzene values of the investigator whose work was to be compared. Since in this case all the observers whose results we shall consider have not determined benzene, it has seemed better to take for K_B the mean of the values calculated from all the reliable *benzene* results by

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capillary rise to be found in the literature, using the observed temperature, 288.5°, for t_c. These mean values of K_B are collected in Table VII.

TABLE VII.—MEAN VALUES OF K_B FROM CAPILLARY RISE.

Ramsay and Shields	$K_B = 2.1012$
Ramsay and Aston	2.1211
Renard and Guye	2.1108
Walden	2.1260
Average,	$K_B = 2.1148$

From the drop weight in milligrams on this tip, then, we can calculate γ, the surface tension in dynes per centimeter at the same temperature, by aid of the relationship

$$\gamma_t^f = \frac{2.1148}{2.3502} w_t = 0.89984 w_t. \qquad (1)$$

Since the volume of a drop, $\frac{w_t}{d_t}$, is proportional to the capillary constant, $a^2 = h \times r$, and this is more directly obtainable from the observed rise in a capillary tube than the surface tension is, for that requires a knowledge of the difference between the density of the liquid and that of the vapor, or of the air saturated with vapor, comparisons can also be made, and at times more satisfactorily, between drop volume and the capillary constant than between drop weight and the surface tension. We would have, then, the relationship

$$a^2 = \text{constant} \times \frac{w_t}{d_t},$$

in which we have only to calculate the value of the "constant" for the standard liquid, *benzene*.

Since $a^2 = h \times r$, we can calculate the value of a^2 from the results of capillary rise, when the height and the radius of the tube are both known. As the comparison of a^2 and w/d must be made at the same temperature, the values of w for benzene must be calculated from the equation

$$w_t = \frac{2.3502\ (288.5 - t - 6)}{\left(\frac{78}{d_t}\right)^{\frac{2}{3}}},$$

which we know from work on other tips holds not only for 60.4° as above, but also at all other temperatures. In Table VIII are given the various values, h, r, w, and d for *benzene* necessary for the calculation of the "constant," together with the mean value of this. All densities here are calculated from the formula

$$d_t = 0.9002145 - 0.00106596t.$$

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TABLE VIII.—VALUES OF THE "CONSTANT" IN a^2 = CONSTANT × $\frac{w_t}{d_t}$ FOR BENZENE.

t_t	h.	r.	w.	d.	$\frac{w}{d}$	a^2.	$\frac{a^2}{w/d}$=constant.
			Ramsay and Shields.				
80	3.945	0.012935	22.744	0.8149	27.910	5.103	0.18284
90	3.772	0.012935	21.433	0.8043	26.648	4.879	0.18309
100	3.603	0.012935	20.139	0.7936	25.377	4.661	0.18367
						Average,	0.18320
			Ramsay and Aston.				
11.2	3.642	0.01843	32.274	0.8883	36.333	6.712	0.18473
46.0	3.213	0.01843	27.346	0.8512	32.126	5.922	0.18432
78.0	2.810	0.01843	23.010	0.8171	28.161	5.179	0.18390
						Average,	0.18432
			Renard and Guye.				
11.4	4.346	0.01522	32.246	0.8881	36.309	6.615	0.18218
31.2	4.120	0.01522	29.417	0.8670	33.918	6.271	0.18482
55.1	3.744	0.01522	26.094	0.8415	31.009	5.698	0.18377
68.5	3.516	0.01522	24.277	0.8272	29.349	5.351	0.18234
78.3	3.385	0.01522	22.969	0.8167	28.124	5.152	0.18319
						Average,	0.18326
			Walden.				
18.1	3.392	0.0193	31.279	0.8809	35.508	6.547	0.18437
38.3	3.157	0.0193	28.417	0.8594	33.067	6.093	0.18427
41.0	3.122	0.0193	28.156	0.8565	32.874	6.026	0.18330
						Average,	0.18398

The mean of all these average values is **0.1837.** For the transformation of the drop weight of ANY liquid in milligrams into the capillary constant at the same temperature, then, we have the relationship

$$a^2 = 0.1837 \times \frac{w_t}{d_t}. \qquad (2)$$

In Table IX are given the values of t_c for water calculated from the drop weights and the normal, benzene, constant, **2.3502.** This is a typical associated liquid, and the calculated value of t_c, as will be observed, increases with the temperature of observation.

Plotting the variation of the drop weight of water with the temperature shows that the relationship is not linear, the temperature coefficient increasing slightly with increased temperature. Treatment of the experimental results by the method of least squares, omitting the weight at 0°, leads to the formula

$$w_t = 84.317 - 0.1719t - 0.000247t^2, \qquad (3)$$

for this tip, between 0° and 77°.

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TABLE IX.—VALUES OF t_c FOR WATER; M = 18.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c from k_B = 2.3502.
0.0	0.99987	84.325	579.22	252.5
1.8	0.99996	84.045	577.26	253.5
4.0	1.00000	83.638	574.45	254.4
6.0	0.99997	83.293	572.09	255.4
7.5	0.99990	83.027	570.29	256.2
13.0	0.99940	82.033	563.65	258.8
15.0	0.99913	81.643	561.07	259.7
17.0	0.99897	81.291	558.71	260.7
19.3	0.99838	80.920	556.38	262.0
22.5	0.99768	80.308	552.43	263.6
25.3	0.99699	79.803	549.21	265.0
27.8	0.99632	79.338	546.26	266.2
30.0	0.99567	78.940	543.75	267.4
36.5	0.99336	77.750	536.39	270.7
40.0	0.99224	77.070	532.09	272.4
45.0	0.99025	76.070	525.89	274.8
55.0	0.98573	74.073	513.65	279.6
60.0	0.98324	73.148	508.10	282.2
70.0	0.97781	71.068	495.47	286.8
77.0	0.97368	69.630	486.82	290.1

Table X, in which the results of the application of this formula are given at the various temperatures, together with the observed values, shows the greatest variation between the calculated and observed values

TABLE X.—THE DROP WEIGHT OF WATER IN MILLIGRAMS.

$$w_t = 84.317 - 0.1719t - 0.000247t^2.$$

t.	w calc.	w obs.	Δ.
0.0	84.317	84.325	+0.008
1.8	84.008	84.045	+0.037
4.0	83.625	83.638	+0.013
6.0	83.277	83.293	+0.016
7.5	83.014	83.027	+0.013
13.0	82.040	82.033	—0.007
15.0	81.682	81.643	—0.039
17.0	81.323	81.291	—0.032
19.3	80.907	80.920	+0.013
22.5	80.324	80.308	—0.016
25.3	79.810	79.803	—0.007
27.8	79.347	79.338	—0.009
30.0	78.938	79.940	+0.002
36.5	77.714	77.750	+0.036
40.0	77.046	77.070	+0.024
45.0	76.081	76.070	—0.011
55.0	74.115	74.073	—0.042
60.0	73.114	73.148	+0.034
70.0	71.051	71.068	+0.017
77.0	69.617	69.630	+0.013

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to be 0.057 per cent., while the general agreement is very much better. In short, then, *we may use the results of this equation in place of the experimental values in all cases of comparison.*

Naturally, the surface tensions calculated from the above drop weights, since they are proportional to them, will also be in curvilinear relationship with the temperature. Unfortunately, the table of values from capillary rise given in Landolt-Börnstein-Meyerhoffer (p. 102, 1905) is made up from the work of Volkmann, 6–30° (1895), and from Brunner (1847) to 80°, and shows the relationship to be nearly linear, and sharply divided into two distinct portions of differing slope, joining at 40°, so that a direct comparison of the results of the two methods could at best show agreement only in places. The values of surface tension, calculated from the equation

$$\gamma_t = 75.872 - 0.1547t - 0.000222t^2, \qquad (4)$$

obtained by multiplying each term of the above drop weight equation by 0.89984, are given for every 5° from 0–80° in Table XI, together with the values to be found in Landolt-Börnstein-Meyerhoffer, and those observed by Ramsay and Shields.

TABLE XI.—SURFACE TENSION OF WATER IN DYNES PER CM.[1]

t.	From eq. (4).	V. & B.	% Δ.	R. & S.
0	75.872	75.49	—0.50	73.21
5	75.092	74.75	—0.46	...
10	74.303	74.01	—0.40	71.94
15	73.501	73.26	—0.33	...
20	72.690	72.53	—0.22	70.60
25	71.867	71.78	—0.12	...
30	71.031	71.03	0.00	69.10
35	70.188	70.29	+0.14	...
40	69.332	69.54	+0.30	67.50
45	68.465	68.6	+0.20	...
50	67.587	67.8	+0.31	65.98
55	66.692	66.9	+0.31	...
60	65.798	66.0	+0.30	64.27
65	64.878	65.1	+0.34	...
70	63.965	64.2	+0.37	62.55
75	63.021	63.3	+0.44	...
80	62.075	62.3	+0.37	60.84

The irregular variation of the values of Volkmann and Brunner from those of drop weight, although not very great, plainly shows that the type of curve expressing their results is quite different from the perfect parabola found for the surface tensions as found from drop weight, the

[1] Magni (*Atti accad. Lincei*, 20, 33 (1911)) finds for water at 18°, by the method based upon the pressure necessary to form an air bubble, the value 73.065 dynes, while equation (4) at this temperature leads to 73.022, a difference of but 0.06%. This is for water when saturated with air in both cases.

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two curves touching only at 30°, while the Ramsay and Shields' values are lower throughout, by about 3.5 per cent. at 0°, and by 2 per cent. at 80°. Such a difference is perhaps to be expected, as far as concerns the results of Ramsay and Shields, for they worked in the absence of air, and at a pressure equal to the vapor pressure of the liquid. It is only at the boiling point, 100°, then, that their conditions would correspond to those under which the drop weight was determined, for then only would the pressure be atmospheric and the liquid in both cases free from air. As will be observed, the agreement improves with increased temperature, so that it is possible that at 100° the values observed would correspond.

Most of the workers, by various methods, who have employed fairly large limits of temperature, have found the same parabolic type of curve representing the relationship of surface tension with temperature, as that found from the drop weight. Weinberg,[1] for example, finds for water, between 1° and 74° the equation

$$\gamma_t = \gamma_0 (1 - 0.0020532t - 0.0000028432t^2).$$

Writing equations (3) and (4) in this form, we obtain

$$w_t = w_0 (1 - 0.0020386t - 0.0000029294t^2)$$

and

$$\gamma_t = \gamma_0 (1 - 0.0020386t - 0.0000029294t^2).$$

Writing the equations in this form, where the value at any temperature is found as a percentage of its value at 0°, enables us to compare the variation with the temperature of two proportional properties which may be expressed in entirely different units, and that without the use of any specific quantities. That the two curves, that from Weinberg and that from drop weight, are in fact perfectly parallel, even though the coefficients of t and t^2 do differ very slightly, can be shown by calculating the values of the function at two extreme temperatures, in terms of its value at 0°. Thus at 20° Weinberg's value of γ is equal to $0.9580 \times \gamma_0$, where the value from drop weight is $0.9578 \times \gamma_0$, while at 80° we have $0.91755 \times \gamma_0$ for Weinberg, as compared to $0.91813 \times \gamma_0$ for the value from drop weight, a difference of but 0.06 per cent. This agreement in relative value is all the more remarkable from the fact that Weinberg used a method based upon the force necessary to draw a copper ring away from the surface of the water, and found an absolute value at 0° considerably larger (7 per cent.) than that from drop weight, *the percentage variation in the surface tension with the temperature, however, being practically exactly identical according to both methods.*

The comparison of the results of the drop weight and capillary rise methods can perhaps be made through the value of the capillary constant,

[1] *Z. physik. Chem.*, 10, 34–50 (1892).

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a^2, which is equal to the height of ascension times the radius of the tube, for, as most observers have noted, this quantity for water stands in linear relationship to the temperature. In Table XII are given the experimental values of the capillary constant, assuming it to be proportional to the drop volume, *i. e.*, from the equation $a_t^2 = 0.1837 \frac{w_t}{d_t}$, together with the corresponding values calculated by aid of the equation

$$a_t^2 = 15.493 - 0.0308t, \qquad (5)$$

obtained by combining the equations $\frac{w_t}{d_t} = 84.337 - 0.1678t$, and $a_t^2 = 0.1837 \frac{w_t}{d_t}$.

TABLE XII.—VALUES OF THE CAPILLARY CONSTANT FOR WATER.

t.	a^2 from (5).	a^2 obs. from (2).	Δ.
0.0	15.493	15.493	0.0
1.8	15.438	15.440	+0.002
4.0	15.370	15.364	—0.006
6.0	15.308	15.301	—0.007
7.5	15.262	15.254	—0.008
13.0	15.093	15.078	—0.015
15.0	15.033	15.011	—0.022
17.0	14.969	14.949	—0.020
19.3	14.899	14.889	—0.010
22.5	14.800	14.787	—0.013
25.3	14.714	14.704	—0.010
27.8	14.637	14.628	—0.009
30.0	14.569	14.564	—0.005
36.5	14.369	14.378	+0.009
40.0	14.261	14.269	+0.008
45.0	14.107	14.112	+0.005
55.0	13.799	13.804	+0.005
60.0	13.645	13.667	+0.022
70.0	13.337	13.352	+0.015
77.0	13.121	13.137	+0.016

It will be observed that although this relation is not perfectly linear, a negative variation existing at one extreme, while a positive one is observed at the other, thus pointing to a slight curvature, it may be considered as linear, without involving unreasonable error.

Writing this equation for a^2 in the percentage form, *viz.*,

$$a_t^2 = a_0^2 (1 - 0.001987t),$$

a_0^2 being equal to 15.493 mm., and comparing it with Weinberg's similar formula

$$a_t^2 = a_0^2 (1 - 0.001975t),$$

we find again, as is to be expected from the similar relationship for surface tension, a perfect and complete parallelism, with respect to the variation with temperature, between the results calculated from drop weight,

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and those, by an entirely different method, of Weinberg. Further, Weinberg finds from the work of eleven of the most reliable observers of capillary rise that the mean temperature coefficient of the capillary constant is 0.00200, as compared to the above value, 0.001987, as found from drop weight, a difference, which for 80° would amount to less than one-tenth of 1 per cent., *i. e.*, that between $0.9400 \times a_0^2$, and $0.9408 \times a_0^2$. Weinberg finds further that the mean value of a_0^2 from the work of thirty of the best observers of capillary rise is 15.350 ± 0.188, while the mean value of all observers, excluding those of eight pioneers, is 15.40, for ninety-six individual determinations, as compared to the value of 15.493 from drop weight. It is to be remembered in this connection that the values of γ and a^2 from drop weight are only relative, which may account for the difference between the drop weight value, based upon the benzene values of four modern, accurate, workers, and the mean of all observers. The absolute value as found from capillary rise is dependent primarily upon the accuracy with which the radius of the capillary tube is measured, and it is thought that the diameters from which the benzene value we have used is calculated are probably more accurate, owing to our refined, present-day methods of measuring small distances, than those upon which the older capillary rise results were based. It is for this reason that it is thought that *the values given above for γ_t and a_t^2 may be regarded as standard, not only as to variation with the temperature, but also in absolute value.*

All attempts to calculate the critical temperature of water by the method employed on the results of Ramsay and Shields by Morgan[1] proved futile, due apparently to the fact that the observations were not carried to a high enough temperature to fix accurately the values of the coefficients of t and t^2. The method of least squares applied to the values of the molecular function $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$ for water lead to the equation

$$\left[w\left(\frac{M}{d}\right)^{\frac{2}{3}}\right]_t = 578.96 - 1.55t - 0.00052t^2,$$

which gives a value of the critical temperature which is absurd. It is significant here that an equation from the Ramsay and Shields values up to 80° only, as these were, and not to 140° as Morgan's were, also leads to an absurd value. It may be said here, as showing the great effect of the high temperatures in fixing the values of the coefficients of the first and second powers of the temperature, that the equation which would practically give the critical temperature, 365°, for water is

$$\left[w\left(\frac{M}{d}\right)^{\frac{2}{3}}\right]_t = 579.22 - 1.0817t - 0.0015t^2,$$

[1] THIS JOURNAL, 31, 309–322 (1909).

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which gives an identical value with experiment at 0° and one of 482.99 at 80°, as compared to the experimental one of 483.03, but which could not be found except with a previous knowledge of the experimental critical temperature. With values at higher temperatures, this equation would not only hold, but would also be the only one that could be found by the method of least squares, and thus would lead, without a knowledge of the experimental value, to the true critical temperature of the liquid. It is quite evident, then, that for associated liquids, results at the higher temperatures must be at hand in order that the method of least squares may lead to coefficients of t and t^2 which are sufficiently accurate to allow the calculation of an unknown critical temperature.

The values of t_c calculated from the experimental values at the various temperatures of observation, by aid of the benzene constant, 2.3502, for ethyl alcohol, methyl alcohol, and acetic acid, are given in Table XIII. As will be observed in all cases, just as with water, the values increase with increased temperature of observation.

TABLE XIII.—VALUES OF t_c FROM $k_B = 2.3502$.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
Ethyl alcohol, M = 46; t_c obs. = 243.1°.				
0	0.8095	25.900	382.82	168.9
10	0.8014	25.008	372.12	174.3
20	0.7926	24.120	361.56	179.8
40	0.7754	22.327	339.61	190.5
50	0.7663	21.473	329.20	196.1
60	0.7572	20.608	318.47	201.5
65	0.7523	20.200	313.52	204.4
70	0.7474	19.828	309.09	207.5
Methyl alcohol, M = 32; t_c obs. = 240°.				
0	0.8100	26.382	306.01	136.2
20	0.7905	24.527	289.16	149.0
30	0.7830	23.603	280.04	155.2
40	0.7745	22.663	270.85	161.3
50	0.7650	21.755	262.15	167.5
Acetic acid, M = 60; t_c = 321.5°.				
20	1.0491	29.889	443.68	214.8
40	1.0284	27.773	417.78	223.8
60	1.0060	25.710	392.47	233.9
70	0.9948	24.700	379.87	237.6

The relationship existing between the drop weight (and also the surface tension, of course) and the temperature for methyl alcohol and acetic acid is very satisfactorily linear, as it also is for ethyl alcohol up to 60°, although at 65° and 70° there is a distinct and sharp curvature, the reason for which is not apparent.

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For methyl alcohol, between 0° and 50°, we have the relationship

$$w_t = 26.382 - 0.0927t = 26.382\ (1 - 0.003514t);$$

for ethyl alcohol, between 0° and 60°,

$$w_t = 25.888 - 0.0883t = 25.888\ (1 - 0.00341t);$$

and for acetic acid, calculated from 20°–70°,

$$w_t = 31.949 - 0.1038t = 31.949\ (1 - 0.00325t).$$

Transforming these equations for drop weights into surface tensions, by multiplication with 0.89984, we find for methyl alcohol

$$\gamma_t = 23.740 - 0.0834t = 23.740\ (1 - 0.003514t);$$

for ethyl alcohol

$$\gamma_t = 23.295 - 0.0795t = 23.295\ (1 - 0.00341t);$$

and for acetic acid

$$\gamma_t = 28.749 - 0.0933t = 28.749\ (1 - 0.00325t),$$

all in dynes per centimeter.

Transforming the drop weights at the various temperatures into drop volumes, by dividing by the density at that temperature, and the linear equation of the variation of this property with the temperature, into that for the capillary constant, by multiplying each term by the factor 0.1837, we find for the above liquids the following equations for the change of a^2, the capillary constant, with the temperature. For methyl alcohol

$$a_t^2 = 5.996 - 0.01543t = 5.996\ (1 - 0.00257t);$$

for ethyl alcohol

$$a_t^2 = 5.876 - 0.01455t = 5.876\ (1 - 0.002476t);$$

and for acetic acid

$$a_t^2 = 5.5027 - 0.0135t = 5.5027\ (1 - 0.00245t).$$

Without taking up too much space in a comparison of the above values of γ and a^2 with those found by other methods and workers, it may be said that for ethyl alcohol Timberg[1] found, by measurement of the radius of curvature of an air bubble under the liquid, the equations

$$\gamma_t = \gamma_0\ (1 - 0.0034t)$$
$$a_t^2 = a_0^2\ (1 - 0.002784t),$$

which shows perfect agreement in temperature coefficient, as far as concerns γ, with the result from drop weight, and differs but slightly, due to the use of different densities probably, from that for a^2; although again, as for water in the case of Weinberg, the zero values are considerably higher, *viz.*, 6.074 for a^2.

Table XIV gives the various values of a^2 at 20° for ethyl alcohol.

[1] *Wied. Ann.*, 30, 545–561 (1887).

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TABLE XIV.—a^2 FOR ETHYL ALCOHOL AT 20°.

Observer.	a^2.
Morgan and McAfee	5.597
Ramsay and Shields	5.663
Magie[1]	5.599
Quincke[1]	5.659
Timberg	5.736
Schiff[2] from 5.5° and 78°	5.721
Renard and Guye[3]	5.709

Only two observers, Ramsay and Shields, and Schiff have studied methyl alcohol, the former at 20° and 70°, and higher temperatures, and Schiff at 7.3° and 64.2°, Schiff's results for the capillary constant from these two temperatures may be expressed by the equation

$$a_t^2 = 6.128 - 0.016t = 6.128\ (1 - 0.0026t);$$

while from Ramsay and Shields can be found

$$a_t^2 = 6.169 - 0.019t = 6.169\ (1 - 0.003t);$$

i. e., Schiff's percentage temperature coefficient is practically identical with that from drop weight, or rather drop volume, while Ramsay and Shields is somewhat higher. In Table XV are compared the values of a^2 for this liquid at three temperatures, which will show the point at which the values of Ramsay and Shields cross those found from the drop weight.

TABLE XV.—VALUES OF a^2 FOR METHYL ALCOHOL.

Observer.	20°.	40°.	50°.
Morgan and McAfee	5.688	5.380	5.226
Schiff	5.808	5.488	5.328
Ramsay and Shields	5.789	5.409	5.219

Acetic acid, also, has been studied only by Schiff and Ramsay and Shields: the former at two temperatures, the latter at 20° and then at 130° and higher. Schiff's results for the capillary constant may be expressed by the equation

$$a_t^2 = 5.627 - 0.015t = 5.627\ (1 - 0.00267t).$$

The values of a^2 for this liquid at 20° are compared in Table XVI.

TABLE XVI.—VALUES OF a^2 AT 20° FOR ACETIC ACID.

Observer.	a^2.
Morgan and McAfee	5.237
Schiff	5.327
Ramsay and Shields	5.019

Here the values from drop weight, as will be observed, lie between

[1] *Wied. Ann.*, 25, 421–437 (1885).
[2] *Ann.*, 223, 69 (1884).
[3] *J. chim. phys.*, 7, 100 (1907).

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those of Ramsay and Shields, the percentage temperature coefficient of Schiff being slightly larger.

All attempts to calculate the critical temperatures of ethyl alcohol and acetic acid, by the method of Morgan,[1] based upon the finding of an equation for the variation of $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$ with the temperature, and involving the temperature and the square of the temperature, failed, owing to the change in the drop weight relation, and also in that of the function, at 60°, for ethyl alcohol, and from the fact that the few points for acetic acid (the highest being 251° below the critical 321°) seemed rather to indicate a linear relationship with the temperature.

In the case of methyl alcohol, just as with water, the equation of a curve could be derived from the experimental critical temperature which agreed well with the experimental results. This equation is

$$w_t = 306.01 - 0.0795t - 0.0017t^2.$$

Morgan's equation (11),[1] based upon the relationship of the coefficients of t and t^2 leads from this equation to a critical temperature of 240°, while his equation (10) based upon the temperature at which the function $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$ becomes zero, leads to 256°, the experimental value being 240°.

The question as to the real molecular weight, or the factor of association, in the case of these liquids has not been considered here, for it can best be treated in a later paper.

Conclusions.

The results of this investigation may be summarized as follows:

1. The drop weights of water, ethyl alcohol, methyl alcohol, and acetic acid have been determined at various temperatures, and equations giving the surface tensions and capillary constants of these liquids calculated from them.

2. It is shown that in each case the new definition of normal molecular weight as a liquid does not hold, for the value of t_c calculated from the normal benzene constant does not remain constant, but increases with an increase in the temperature of observation. These liquids therefore, according to that definition, are not normal, but associated.

3. It is again shown that for finding either surface tension or the capillary constant of a liquid, the drop weight method is more consistent than any other, leading not only to a smaller variable error, but probably also to a truer absolute value.

LABORATORY OF PHYSICAL CHEMISTRY.

[1] *Loc. cit.*

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HEATS OF REACTION IN NON-AQUEOUS SOLUTIONS.

By J. Howard Mathews.

Received May 20, 1911.

Measurements of heats of reaction have long been considered of fundamental importance in thermo-chemistry, and of late years have played a considerable part in the theory of solutions. So far as the writer is aware, however, nothing has been published concerning the study fo heats of reaction in other solvents than water. A few years ago Dr. F. L. Shinn, at the suggestion of Professor Kahlenberg, made some preliminary experiments along this line in this laboratory. The results of their work indicated that the solvent used seemed to influence the magnitude of the thermal effect produced. It is the purpose of our investigations, of which this paper describes only the preliminary part, to study various reactions in different solvents to ascertain what part the solvent plays in such reactions and perhaps to throw some further light on the somewhat perplexing problem of solutions.

In this paper but one reaction will be considered—the neutralization of pyridine (1 mol.) by acetic acid (1 mol.)—the heat of reaction having been measured in a number of solvents. The heat evolved by the reaction of the pure substances in the absence of any solvent was also measured.

The exact ratio of pyridine to acetic acid in pyridine acetate is immaterial for the case in hand, the essential condition being that the reaction be the same in each case. Therefore the ratio *one* mol. of pyridine to *one* of acetic acid was adopted, and great care was used to see that this ratio was maintained exactly. The product of this reaction is, fortunately, a liquid; and it is soluble in the solvents used, thus obviating complications due to precipitation and corrections therefor.

The object of this preliminary work was to obtain a comparison of values for the different solvents, keeping the conditions the same in each case, rather than to furnish absolute values of heats of neutralization as they are ordinarily measured. Ordinarily the acid and base are each dissolved in a large excess of solvent, the resulting solutions being of equal molecular concentration. These two solutions, when mixed, then give a certain quantity of heat, which, when gram equivalents are taken, is known as the heat of neutralization. In the first series of determinations to be described the experimental conditions were somewhat different. The base—pyridine—was dissolved in the solvent in question and the pure acid (not in solution) was run into this solution. Three procedures naturally presented themselves. Either the weight or volume of solvent might be kept constant for all the different solvents, or equimolecular quantities of the different solvents might be taken. The first alternative was chosen for the preliminary work, and in each case 96.4

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grams of the solvent contained one molecule of pyridine. This is a much more concentrated solution than those ordinarily used. The small heat effect produced by this reaction, together with the cost of the materials, almost precludes the usual procedure. However, some measurements made in the usual way will be carried out.

Materials Used.—Naturally great care was exercised in the preparation of the materials used. For the most part they were substances which present no especial difficulties in purification.

Pyridine.—The pyridine used was Merck's "C. P." It was dried for weeks over fused caustic potash, after which potassium permanganate was added and the mixture boiled under a reflux condenser for several hours for the purpose of destroying the picolines and higher homologs. After this treatment it was distilled from the permanganate. The sample used for the measurements of the first series boiled at 114°–115° at 736 mm.

Acetic Acid.—Glacial acetic acid (99 per cent.) was fractionally recrystallized until a triplicate analysis showed it to be 100 per cent. pure.

Acetone.—The acetone available was of excellent quality. It had stood over anhydrous copper sulfate for several weeks. Upon distillation several liters were obtained within a temperature range of 0.05°. The boiling point of the sample used was 54.4° at 725 mm.

Benzene.—The benzene used (Merck's recrystallized) was fractionally recrystallized and redistilled. Its constancy of boiling point (78.0–78.2° at 737 mm.) showed it to be very pure.

Carbon Tetrachloride and Nitrobenzene.—These were both fractionally distilled, no further treatment being necessary, judging from the constancy of their boiling points. The carbon tetrachloride boiled at 74.5°–74.8° at 743 mm., and the nitrobenzene at 209.0° at 740 mm.

Carbon Bisulfide.—The carbon bisulfide had stood over copper foil for some time. It was then fractionated by distillation, using an electrical heating device to prevent superheating. The fraction used boiled at 46.3° at 751 mm.

The Alcohols.—The methyl alcohol had stood over anhydrous copper sulfate for several months. It was fractionated by distillation and the distillate showed no coloration upon standing with anhydrous copper sulfate. The fraction used boiled between 64.3°–64.5° at 742.5 mm.

The ethyl alcohol after standing over anhydrous copper sulfate for several months was distilled. The best boiling fractions were mixed and redistilled with metallic sodium. A distillate of almost constant boiling point (77.7° at 740 mm.) was obtained.

The isoamyl alcohol was subjected to fractional distillation only. Its very constant boiling point (129.2°–129.3° at 750 mm.) showed no other treatment to be necessary.

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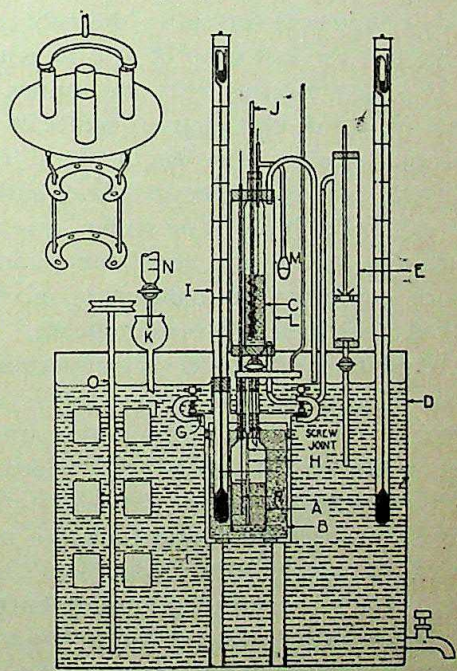
Ethyl Acetate.—Kahlbaum's C. P. ethyl acetate was treated with a large quantity of phosphorus pentoxide, and after standing a few days it was distilled therefrom. The fraction used boiled at 75.9°–76.1° at 743 mm.

Chloroform.—The chloroform was fractionated by distillation and that portion having a boiling point of 60.15°–60.2° at 744 mm. was used.

Method.—The method of measurement of heat values was practically that developed by Richards and Rowe[1] for the measurement of specific heats of liquids. The new form of adiabatic bath described by Richards and Burgess[2] and by Richards and Jesse[3] was used instead of the earlier form. The new bath was found to be far superior, as it simplifies the manipulations greatly and makes possible a much more exact control of temperature. The accompanying diagram shows the apparatus in cross section.

The reaction takes place in the small platinum bottle *A*, which is suspended in a weighed amount of water in the platinum vessel *B* (of about 600 cc. capacity) constituting the calorimeter proper. The solution of the base was placed in the platinum bottle and the acid run into it from the jacketed cylindrical separatory funnel, *C*, placed above. In order that the initial temperature of acid and alkali might be the same at the moment of mixing, the alkali contained in the large outer bath *D* was caused to circulate through the jacket *L*, surrounding the funnel containing the acid, by means of the small pump *E*, run by an electric motor. In this way the temperature of the acid, which was constantly stirred by means of a small spiral platinum stirrer surrounding the thermometer, could be brought quickly to the temperature of the mixture in the calorimeter. The temperature of the acid was taken by means of an excellent thermometer *I*, graduated to 0.01° and capable of being read to 0.001°. This thermometer had been compared previously with the Beckmann at each 0.1° and a table was always at hand giving



[1] *Z. physik. Chem.*, 64, 187 (1908).
[2] THIS JOURNAL, 32, 431 (1910).
[3] *Ibid.*, 32, 268 (1910).

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the readings of one thermometer in terms of the other. It was therefore possible to ascertain at a glance when the temperature of alkali and acid were the same. Having brought the temperature of each to the same point before mixing, no correction for difference in temperature was necessary. In a number of these preliminary measurements this ideal condition was not realized exactly, but in such cases the correction, always slight in value, was accordingly made.

At the moment when it was desired that the substances react, the circulation of alkali through the jacket around the acid compartment was stopped by closing the valve on the pump, and the large bored stopcock on the acid funnel *C* was opened. Sulfuric acid was run from a buret *N* into the outer compartment at such a rate that the temperatures of the mixture within the calorimeter and the contents of the outer compartment, as indicated by the two Beckmann thermometers whose zeros had been set together, rose simultaneously. Loss or gain of heat by the calorimeter through radiation was thus eliminated. Not more than two seconds were required for the acid to run into the platinum bottle. A few moments thereafter the rubber bulb *M* was compressed so as to force out the last drop of acid hanging in the delivery tube.

It seems unlikely that an appreciable error could have arisen from gain or loss of heat in transference of the acid into the bottle for the following reasons: The length of the delivery tube exposed between the jacketed acid container and alkali bath below was not greater than three-fourths of an inch. The system was always at about the room temperature and had always stood for a considerable time, with everything in place, preceding the moment of mixing. The delivery of acid into the alkali was practically instantaneous.

The rate of stirring is very important, as has been pointed out by Richards and Burgess.[1] In the earlier part of this work somewhat erratic results were obtained, which were traced later to inefficient stirring. In the work here described the calorimeter stirrers, both in calorimeter and in bottle, were driven at the rate of from 70 to 80 strokes per minute, thus assuring prompt and thorough mixing. The maximum rise of temperature was generally reached in about five or six minutes after mixing. The stirrer in the platinum bottle *P* consisted of two disks of sheet platinum attached to a short, stout platinum rod suspended from the plunger of the calorimeter stirrer by means of a fine platinum wire. The calorimeter stirrer (shown in detail in the smaller diagram) consisted of two flat, perforated rings of pure silver held in position by two silver rods, each of which screwed into a thin rod of celluloid attached to the cross-bar above. The joint between silver and celluloid was just above the surface of the water. The celluloid rods were used to reduce the

[1] *Loc. cit.*

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liability of conduction of heat into or out of the calorimeter, and to render the calculation of the water equivalent more certain.

The acid in the funnel C was stirred by means of a thick spiral of braided platinum wire surrounding the thermometer and attached to the plunger of the calorimeter stirrer.

Some of the liquids used were quite volatile. Care was taken to prevent evaporation, not only because of the resulting loss of material but also in order to prevent the thermal effect which would be produced by such evaporation. The thermometer and delivery tube passed through tightly fitting corks. The fine platinum wire from the bottle stirrer passed through a glass guiding tube which was of very small bore at each end. The celluloid rods of the calorimeter stirrer worked through corked sleeves, which reduced the size of the necessary opening to a minimum. By using these precautions no difficulty from evaporation of material was experienced.

The outer alkali compartment was stirred by a powerful 10-bladed stirrer, *O*, as indicated, run at a rate of several hundred revolutions per minute. Complete admixture of the concentrated sulfuric acid with the alkali liquid was practically instantaneous. The whole system of stirrers and the pump were driven by a $^1/_{30}$ h. p. electric motor, through a suitable adjustment of pulleys. The speed of the motor was controlled by a rheostat with sliding contact.

The calorimeter thermometer used was an excellent, large-bulbed Beckmann of Goetze's manufacture, having a clearly marked scale. It was most carefully standardized by comparison with a 0.01° thermometer which had been standardized by the Reichsanstalt. During the comparison both thermometers were placed in the adiabatic calorimeter with bulbs close together. Readings were recorded only after they had become constant on each thermometer. The scales were compared at intervals of every 0.1° throughout the entire length of the Beckmann scale. Two such series of comparisons were made in the same manner and from the average of these nearly identical series a curve and table for the instrument were prepared. The excellent concordance of values obtained for the amount of heat liberated by the neutralization of a definite quantity of a certain strength hydrochloric acid solution, to be described later, and the additional fact that these measurements were made at slightly different parts of the Beckmann scale, attested to the fact that the standardization was most carefully made and was satisfactory.

Since there is no indicator known for the reaction between pyridine and acetic acid it was necessary to rely on weighing to ascertain the end-point, *i. e.*, to ascertain whether the ratio of one mol. of pyridine to one mol. of acetic acid had been maintained exactly. The procedure was as follows: Exactly 19.77 grams of pyridine (*i. e.*, 0.25 mol.) were weighed

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out in the platinum bottle. 24.1 grams of the solvent were then added. 14.55 cc. of pure acetic acid were run into the jacketed acid compartment. After the determination had been made the stirrer, bottle and contents were again weighed in order to determine how much acid had actually been used in the reaction. Care was taken to keep this amount as constant as possible, because further addition of acid would be accompanied by a heat effect. It was found possible to deliver almost exactly the theoretical quantity (15.01 grams) to the platinum bottle.

In order to calculate the heat of neutralization we must know the water equivalent of the solution formed in the platinum bottle, since this is also warmed by the reaction and therefore takes up a part of the heat liberated. This makes necessary a determination of the specific heat of the mixture. The manipulation was the same as for the heat of neutralization, except that a weighed quantity of the pyridine acetate solution was placed in the platinum calorimeter and an accurately weighed quantity (40.86 grams) of a 1.366 *N* hydrochloric acid solution was always placed in the platinum bottle; and the acid was just neutralized by running into it the requisite quantity of 2.732 N sodium hydroxide solution. After the rise in temperature had been recorded the apparatus was taken apart, the bottle, stirrer and contents weighed and the very slight excess of sodium hydroxide solution determined by titration. The quantity of sodium hydroxide solution used was always so adjusted that the neutralization was complete and that the excess should not amount to more than 0.1 cc. It was in fact generally less. The heat of dilution of this small amount of sodium hydroxide solution is so small as to be negligible.

In order to determine the exact quantity of heat liberated by the exact neutralization of 40.86 grams of this particular acid solution, the following series of four determinations were made, the first of which is given in detail to show the method of calculation:

TABLE I.

DETERMINATION OF AMOUNT OF HEAT LIBERATED BY EXACT NEUTRALIZATION OF 40.86 GRAMS OF 1.366 *N* HYDROCHLORIC ACID.

Data concerning temperature:	
Initial temperature of sodium hydroxide solution	0.949°
Initial temperature of calorimeter	0.949°
Final temperature of calorimeter	2.412°
Rise in temperature during experiment	1.463°
Data concerning heat capacity, expressed in terms of water equivalent:	
Water in calorimeter	450.00 grams
Calorimeter and fittings, equivalent to	8.11 grams
62.96 grams of sodium chloride solution (sp. ht. 0.94)	59.18 grams
Total water equivalent	517.29 grams

Total heat liberated = 517.29 × 1.463 = 756.79 cals.

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The data for the entire series of four determinations are given in the following table:

TABLE II.

No.	Total water equivalent. Grams.	Initial temp. NaOH.	Initial temp. calorimeter.	Rise in temperature.	Total heat liberated. Cals.
1	467.18	0.816°	0.816°	1.620°	756.83
2	517.29	0.949°	0.949°	1.463°	756.79
3	517.26	0.771°	0.772°	1.463°	756.75
4	517.26	0.670°	0.672°	1.463°	756.75
Average					756.78

Examples of the method of handling the data for the determination of heat of reaction and the specific heat of the resulting mixture will also be given at this point for the purpose of illustration. The data for specific heat are given first, as these values must be used in the other calculation:

TABLE III.

SPECIFIC HEAT OF PYRIDINE ACETATE (1 MOL. PYRIDINE + 1 MOL. ACETIC ACID) DISSOLVED IN 96.4 GRAMS OF CARBON TETRACHLORIDE.

Weight of 1.366 *N* hydrochloric acid solution used	40.86 grams
Excess of sodium hydroxide (determined by titration)	0.05 cc.
Weight of pyridine acetate solution taken	500.00 grams
Data concerning temperature:	
Initial temperature of sodium hydroxide	1.289°
Initial temperature of calorimeter	1.287°
Final temperature of calorimeter	4.348°
Rise in temperature during experiment	3.061°
Data concerning heat capacity, expressed in terms of water equivalent:	
62.83 grams of sodium chloride solution (sp. ht. 0.94), equivalent to	59.06 grams
Calorimeter and fittings, equivalent to	8.11 grams
Total water equivalent	67.17 grams

Heat absorbed exclusive of pyridine acetate solution = 67.17 × 3.601 = 205.61 cals.
Heat liberated by neutralization of 40.86 grams acid = 756.78 cals.
Heat taken up by pyridine acetate solution = 756.78 — 205.61 = 551.17 cals.
Specific heat of solution = 551.7 ÷ (500.00 × 3.061) = 0.3601.

TABLE IV.

DETERMINATION OF AMOUNT OF HEAT LIBERATED BY NEUTRALIZATION OF 1 MOL. OF PYRIDINE IN 96.4 GRAMS OF CARBON TETRACHLORIDE BY 1 MOL. OF ACETIC ACID.

Weight of pyridine taken	19.77 grams
Weight of carbon tetrachloride taken	24.14 grams
Weight of acetic acid used	15.02 grams
Theoretical quantity of acetic acid required	15.01 grams
Data concerning temperature:	
Initial temperature of acetic acid	1.016°
Initial temperature of calorimeter	1.016°
Final temperature of calorimeter	2.152°
Rise of temperature during experiment	1.136°

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Data concerning heat capacity, expressed in terms of water equivalent:

Water in calorimeter	450.00 grams
58.93 grams of pyridine acetate solution (sp. ht. 0.3603), equivalent to	21.23 grams
Calorimeter and fittings, equivalent to	8.11 grams
Total water equivalent	479.34 grams

Heat evolved by the reaction = 479.34 × 1.136 = 544.54 cals.

Heat evolved by neutralization of 1 mol. pyridine in 96.4 grams of carbon tetrachloride by 1 mol. of acetic acid = 4 × 544.54 = 2177.2 cals.

TABLE V.

DATA FOR THE DETERMINATION OF SPECIFIC HEATS OF THE SOLUTIONS FORMED IN THE PLATINUM BOTTLE DURING NEUTRALIZATION EXPERIMENTS.

The quantity of acid solution used was 40.86 grams in each case.

Solvent.	Weight of solution taken.	Initial temp. of alkali.	Initial temp. of calorimeter.	Heat brought in by NaOH.	Rise in temp.	Water equivalent.	Sp. ht.
None	450.00	0.930°	0.933°	.....	2.827°	67.27	0.4454
None	450.00	1.100°	1.098°	.....	2.826°	67.22	0.4457
Average							0.4455
Acetone	450.00	0.052°	0.250°	.....	2.635°	67.30	0.4887
Acetone	450.00	0.712°	0.715°	.....	2.636°	67.23	0.4886
Average							0.4886
Water	450.00	1.280°	1.284°	.....	1.918°	67.12	0.7268
Water	450.00	1.005°	1.006°	.....	1.909°	67.37	0.7312
Water	450.00	1.391°	1.385°	+0.12	1.903°	67.24	0.7344
Water	450.00	1.053°	1.053°	.....	1.911°	67.25	0.7306
Average							0.7307
Benzene	450.00	1.482°	1.477°	.....	2.841°	67.26	0.4426
Benzene	450.00	2.031°	2.021°	+0.20	2.835°	67.25	0.4439
Benzene	450.00	2.387°	2.384°	.....	2.826°	67.22	0.4457
Average							0.4441
Carbon tetrachloride	500.00	1.577°	1.580°	.....	3.057°	67.27	0.3605
Carbon tetrachloride	500.00	1.289°	1.287°	.....	3.061°	67.17	0.3601
Average							0.3603
Nitrobenzene	500.00	1.788°	1.795°	—0.14	2.744°	67.23	0.4170
Nitrobenzene	500.00	2.459°	2.459°	.....	2.741°	67.24	0.4177
Average							0.4173
Carbon bisulfide	450.00	0.969°	0.970°	.....	3.204°	67.22	0.3755
Carbon bisulfide	450.00	0.594°	0.600°	.....	3.198°	67.20	0.3765
Average							0.3760

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TABLE V (*Continued*).

Solvent.	Weight of solution taken.	Initial temp. of alkali.	Initial temp. of calorimeter.	Heat brought in by NaOH.	Rise in temp.	Water equivalent.	Sp. ht.
Ethyl acetate.....	450.00	0.984°	0.981°	.....	2.723°	67.23	0.4682
Ethyl acetate.....	450.00	1.339°	1.339°	.....	2.717°	67.21	0.4696
Average.....							0.4689
Methyl alcohol.....	450.00	1.038°	1.040°	.....	2.490°	67.11	0.5263
Methyl alcohol.....	450.00	0.626°	0.627°	.....	2.491°	67.23	0.5257
Average.....							0.5260
Ethyl alcohol.....	450.00	1.377°	1.382°	—0.22	2.483°	67.22	0.5275
Ethyl alcohol.....	450.00	1.219°	1.216°	.....	2.488°	67.18	0.5267
Average.....							0.5271
Isoamyl alcohol.....	450.00	0.937°	0.935°	.....	2.605°	67.27	0.4961
Isoamyl alcohol.....	450.00	0.956°	0.956°	.....	2.600°	67.28	0.4973
Average.....							0.4967

The data concerning the determinations of the quantity of heat evolved by the addition of 1 mol. of acetic acid to 1 mol. of pyridine dissolved in 96.4 grams of solvent for the different solvents used are given in the following table:

TABLE VI.

Solvent.	Weight of Solvent.	Initial temp. of acid.	Initial temp. of calorimeter.	Heat brought in by acid.	Rise in temp.	Water equivalent.	Heat evolved.	Heat evolved for 1 mol.
None.....	.....	0.893°	0.852°	+0.64	2.336°	489.23	1142.2	2284.4
None.....	.....	1.715°	1.690°	+0.37	2.339°	489.20	1143.8	2287.6
None.....	.....	1.093°	1.029°	+0.94	2.339°	489.09	1143.1	2286.2
Average.....								2286.1
Weight of pyridine used in above determinations = 39.54 grams.								
Weight of pyridine used in succeeding determinations = 19.77 grams.								
Acetone.....	24.00	1.936°	1.857°	+0.58	1.080°	486.87	525.2	2100.8
Acetone.....	24.10	0.757°	0.734°	+0.17	1.077°	486.89	524.2	2096.8
Acetone.....	24.10	0.791°	0.768°	+0.17	1.081°	486.89	526.1	2104.4
Average.....								2100.6
Water.....	24.14	2.193°	2.204°	—0.09	0.876°	501.34	439.3	1757.2
Water.....	24.13	1.483°	1.492°	—0.07	0.877°	501.28	439.7	1758.8
Average.....								1758.0
Benzene.....	24.11	0.542°	0.541°	.....	1.118°	484.29	541.4	2165.6
Benzene.....	24.10	1.039°	1.042°	.....	1.120°	484.27	542.4	2169.6
Benzene.....	24.12	1.197°	1.200°	.....	1.120°	484.33	542.4	2169.6
Average.....								2168.3

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TABLE VI (*Continued*).

Solvent.	Weight of solvent.	Initial temp. of acid.	Initial temp. of calorimeter.	Heat brought in by acid.	Rise in temp.	Water equivalent.	Heat evolved.	Heat evolved for 1 mol.
Carbon tetrachloride.....	24.11	1.016°	1.016°	.....	1.136°	479.34	544.5	2177.0
Carbon tetrachloride.....	24.11	0.945°	0.933°	+0.09	1.138°	479.35	545.4	2181.6
Carbon tetrachloride.....	24.11	1.208°	1.196°	+0.09	1.134°	479.35	543.5	2174.0
Average.....								2177.5
Nitrobenzene...	24.10	2.027°	2.022°	+0.04	1.194°	482.71	576.3	2305.2
Nitrobenzene...	24.11	2.031°	2.029°	.....	1.194°	482.71	576.4	2305.6
Average.....								2305.4
Carbon bisulfide	24.10	0.610°	0.607°	.....	1.070°	480.25	513.9	2055.6
Carbon bisulfide	24.10	0.622°	0.618°	.....	1.070°	480.25	513.9	2055.6
Average.....								2055.6
Ethyl acetate..	24.10	0.727°	0.727°	.....	1.165°	485.78	565.9	2263.6
Ethyl acetate..	24.10	0.803°	0.799°	.....	1.165°	485.77	565.9	2263.6
Average.....								2263.6
Methyl alcohol..	24.10	0.834°	0.834°	.....	0.591°	489.17	289.1	1156.4
Methyl alcohol..	24.11	0.964°	0.964°	.....	0.590°	489.12	288.6	1154.4
Average.....								1155.4
Ethyl alcohol...	24.10	2.449°	2.455°	—0.04	0.640°	489.18	313.1	1252.4
Ethyl alcohol...	24.10	1.931°	1.873°	+0.42	0.642°	489.17	313.6	1254.4
Average.....								1253.4
Isoamyl alcohol	24.10	0.819°	0.824°	.....	0.841°	487.44	409.9	1639.6
Isoamyl alcohol	24.10	0.665°	0.665°	.....	0.841°	487.42	409.9	1639.6
Average.....								1639.6

For convenience in reference the final results for each solvent used in the first series are summarized in the following table:

TABLE VII.

Solvent.	Sp. ht.	Heat evolved for 1 mol. of pyridine. Cals.
None.....	0.4455	2286.1
Acetone.....	0.4886	2100.6
Water.....	0.7307	1758.0
Benzene.....	0.4441	2168.3
Carbon tetrachloride.....	0.3603	2177.5
Nitrobenzene.....	0.4173	2305.4
Carbon bisulfide.....	0.3760	2055.6
Ethyl acetate.....	0.4689	2263.6
Methyl alcohol.....	0.5260	1155.4
Ethyl alcohol.....	0.5271	1253.4
Isoamyl alcohol.....	0.4967	1639.6

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It will be observed that in but one instance, *viz.*, nitrobenzene, was the heat evolved greater than in the case where no solvent was used. It is also interesting to note that the value obtained with water as the solvent is considerably less than the values for the other solvents, excepting the alcohols, which are not comparable because of esterification. The considerable difference in the values obtained with different solvents seems to indicate that the role of the solvent cannot be neglected, *i. e.*, it is not justifiable to think of the reaction as taking place quite independently of the solvent.

In the case of the alcohols it was to be expected that the values would be quite different from the others since there is the possibility that the acetic acid would be partially taken up by the solvent, to form the corresponding ester, thus leaving the pyridine incompletely neutralized. In this connection it is interesting to note that in the case of ethyl acetate, where no such side reaction is possible, the value obtained is approximately the same as that where no solvent was used. Furthermore, as we go up in the series of alcohols the values become higher, as would be expected, since the tendency for the solvent to be reacted upon by the acid becomes less, and the reaction taking place is more nearly the action of the acid on the pyridine alone.

In the case of carbon bisulfide, benzene, ethyl acetate and carbon tetrachloride no side reactions would be expected, and in these cases, together with that of acetone, the values obtained are more nearly of the same order as the value obtained where no solvent was used, the differences probably being due in great measure to differences in heats of solution of the pyridine acetate formed. In order that the acetic acid may act upon the dissolved pyridine, the latter must be taken away from the solvent, and it is only natural that the pyridine would be held more tenaciously by some solvents than by others, and, therefore, that more energy would be required to effect this separation in some cases than in others. The pyridine acetate formed by the reaction in dissolving in different solvents would be likely to produce heat effects of different magnitude. It is therefore not at all surprising that the values fluctuate from solvent to solvent as they do.

Second Series.

In the second series of measurements the method of operation was changed so as to conform more nearly to the usual procedure, in that both the acid and the base were dissolved in the solvent before neutralization took place, the concentration of both the acid and base in the solvent being precisely the same. The concentration adopted was .1 mol. in 100 grams of solvent.

The requisite quantity of pyridine, *viz.*, 19.77 grams (0.25 mol.), was weighed out into the platinum bottle and exactly 25.00 grams of the

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solvent added. The acid solution was prepared similarly and run into the jacketed acid compartment, a very slight, determined excess over the theoretical amount being added to make up for the loss of liquid remaining on the walls when this compartment was emptied into the bottle beneath. After the neutralization had taken place and the temperature data were obtained the solution in the platinum bottle was carefully weighed to ascertain whether the proper quantity of acid solution had been used, and also in order that the water equivalent of the solution formed might be calculated exactly. The remainder of the calculation was precisely the same as those in the first series and therefore need not be repeated.

The materials used were purified with great care, as before. The pyridine was digested with barium oxide[1] for a number of hours before dis-

TABLE VIII.

Solvent.	Weight of solution in calorimeter.	Initial temp. of NaOH.	Initial temp of calorimeter.	Rise in temp. during expt.	Total water equivalent.	Sp. ht.
Water	480.0	0.766°	0.766°	1.660°	67.74	0.8087
Water	480.0	0.728°	0.730°	1.656°	67.73	0.8110
Average						0.8099
Acetone	420.0	0.567°	0.567°	2.705°	67.72	0.5048
Acetone	420.0	0.019°	0.016°	2.706°	67.66	0.5048
Average						0.5048
Chloroform	550.0	0.845°	0.849°	2.932°	67.61	0.3464
Chloroform	550.0	1.003°	1.003°	2.928°	67.71	0.3468
Average						0.3466
Carbon tetrachloride	490.0	1.501°	1.501°	3.384°	67.75	0.3181
Carbon tetrachloride	485.0	1.879°	1.881°	3.389°	67.79	0.3207
Average						0.3194
Benzene	400.0	0.661°	0.661°	3.133°	67.68	0.4347
Benzene	400.0	0.535°	0.535°	3.140°	67.61	0.4335
Average						0.4341
Ethyl acetate	400.0	1.289°	1.287°	2.954°	67.77	0.4710
Ethyl acetate	400.0	0.017°	0.017°	2.962°	67.68	0.4695
Ethyl acetate	400.0	0.760°	0.760°	2.946°	67.66	0.4731
Ethyl acetate	400.0	0.540°	0.539°	2.970°	67.71	0.4677
Average						0.4703

(It should be noted that in this series the temperatures of acid and base were so nearly the same that no correction was necessary.)

[1] Wilcox, *J. Physic. Chem.*, 14, 576 (1910).

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tillation in order to dry it more thoroughly. The product so obtained boiled very constantly, the fraction used coming over between 113.8° and 114.3° at 729 mm.

The data concerning the specific heats of the solutions formed in the neutralization experiments appear in Table VIII. The quantity of hydrochloric acid used was 40.86 grams in every case.

In the following table are given the data concerning the determination of the quantity of heat evolved by the addition of 1 mol. of acetic acid + 100 grams of solvent to 1 mol. of pyridine + 100 grams of solvent. In each determination exactly 19.77 grams of pyridine + 25.00 grams of solvent were taken, and the weight of water in the calorimeter was, in each case, 450.00 grams:

TABLE IX.

Solvent.	Initial temp. of calorimeter.	Initial temp. of acid solution.	Rise in temp. during expt.	Sp. ht. of solution formed.	Weight of solution formed.	Total water equivalent.	Heat evolved.	Heat evolved for 1 mol.
Water	1.121°	1.121°	1.289°	0.8099	84.78	527.22	679.6	2718.4
Water	1.444°	1.446°	1.286°	0.8099	84.72	527.18	678.0	2712.0
Average								2715.2
Acetone	0.659°	0.660°	0.896°	0.5048	84.72	501.33	449.2	1796.8
Acetone	0.657°	0.656°	0.894°	0.5048	84.77	501.35	448.2	1792.8
Average								1794.8
Chloroform	0.668°	0.668°	1.206°	0.3466	84.51	487.85	588.4	2353.6
Chloroform	0.478°	0.478°	1.211°	0.3466	84.59	487.88	590.8	2363.2
Average								2358.4
Carbon tetrachloride	0.818°	0.818°	1.138°	0.3194	84.74	485.63	552.5	2210.0
Carbon tetrachloride	0.822°	0.822°	1.138°	0.3194	84.81	485.65	552.7	2210.8
Average								2210.4
Benzene	0.431°	0.431°	1.146°	0.4341	84.82	495.38	567.7	2270.8
Benzene	0.507°	0.506°	1.150°	0.4341	84.74	495.35	569.6	2278.4
Average								2274.6
Ethyl acetate	0.363°	0.365°	1.072°	0.4703	84.82	498.45	534.3	2137.2
Ethyl acetate	0.227°	0.227°	1.075°	0.4703	84.79	498.43	535.8	2143.2
Average								2140.2

(It will be noted that in all the determinations reported in the above table the temperatures of acid and base were so nearly the same that no correction was necessary.)

For convenience in reference the final results of this series are summarized in the following table:

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TABLE X.

Solvent	Sp. ht. of solution formed.	Heat evolved in neutralization. 1 mol. of pyridine.
Water	0.8099	2715.2
Acetone	0.5048	1794.8
Chloroform	0.3466	2358.4
Carbon tetrachloride	0.3194	2210.4
Benzene	0.4341	2274.6
Ethyl acetate	0.4455	2286.1
None[1]	0.4703	2140.2

It is very evident that the value of the thermal effect produced when pyridine and acetic acid react in different solvents is dependent on the solvent used. Indeed the differences are not very considerable except for the solvents water and acetone, but still they are far greater than the experimental error. Naturally the question arose as to whether these differences might not be due, in considerable part at least, to differences in the heat of solution of the resulting pyridine acetate in the differ-

TABLE XI.

DATA CONCERNING MEASUREMENTS OF HEATS OF SOLUTION.

Solvent.	Weight of solution formed. Grams.	Total water equivalent. Grams.	Rise in temperature.	Heat evolved per mol. Cals.
Water	84.68	527.15	+0.913°	+1925.2
Water	84.77	527.21	+0.916°	+1931.6
Average				+1928.4
Acetone	84.47	501.20	—0.165°	— 330.7
Acetone	84.75	501.34	—0.165°	— 330.8
Average				— 330.75
Chloroform	84.49	487.84	+0.618°	+1205.9
Chloroform	84.49	487.84	+0.618°	+1205.9
Average				+1205.9
Carbon tetrachloride	84.53	485.56	—0.055°	— 106.8
Carbon tetrachloride	84.57	485.58	—0.055°	— 106.8
Average				— 106.8
Benzene	84.50	495.24	—0.103°	— 204.0
Benzene	84.58	495.28	—0.106°	— 210.0
Average				— 207.0
Ethyl acetate	84.71	498.40	—0.119°	— 237.2
Ethyl acetate	84.54	498.33	—0.118°	— 235.2
Average				— 236.2

[1] Value taken from first series, for comparison.

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ent solvents. Consequently a series of determinations of the heat of solution of pyridine acetate in these different solvents were undertaken, the results of which, together with the data, appear in Table XI.

In these measurements the concentration of the final solution was the same as in the neutralization determinations. Fifty grams of the solvent were weighed out into the platinum bottle and the requisit quantity of pyridine acetate was placed in the jacketed compartment above so as to deliver 0.25 mol. into the solvent when temperature equilibrium had been attained.

The following table gives the values for the heats of neutralization after correction has been made for the heat absorbed or evolved in the process of solution of the pyridine acetate formed in the reaction, together with the uncorrected values, and the specific heats of the solutions:

TABLE XII.

SUMMARIZED TABLE.

Solvent.	Sp. ht. of solution formed.	Apparent heat of neutralization. Cals.	Heat of solution of acetate. Cals.	Heat of neutralization (corrected) Cals.
None	0.4469	2279.6	.....	+2279.6
Water	0.8099	2715.2	+1928.4	+ 786.8
Acetone	0.5048	1794.8	— 330.8	+2125.6
Ethyl acetate	0.4703	2140.2	— 236.2	+2376.4
Benzene	0.4341	2274.7	— 207.0	+2481.7
Chloroform	0.3466	2358.4	+1205.9	+1152.5
Carbon tetrachloride	0.3194	2210.4	— 106.8	+2317.2

It will be noted at once that the values for the heats of solution in the various solvents are not only very different but are sometimes of opposite sign, the individual values varying from +1928 cals. to —331 cals.

Furthermore, when the individual values for the heats of neutralization are corrected for the thermal effect produced by the solution of the pyridine acetate formed, the resulting numbers do not agree as well as before the correction was made. Naturally the percentage error is considerably greater in the measurements of the heats of solution, because the thermal effect is so small, yet these discrepancies are by no means to be attributed to experimental error, for the latter are of far lesser magnitude.

It therefore becomes evident that the amount of heat given up in the reaction between pyridine and acetic acid in these various solvents is not a constant quantity, and that the thermal effect is sometimes greater and sometimes less than when the two pure substances interact with each other in the absence of any solvent.

These differences cannot be explained by differences in electrochemical behavior, for in the case of all the solvents other than water and acetone the solutions are practically insulators. The specific conductivities of pyridine acetate solutions in the various solvents used were determined,

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and the data appear in the following table. The concentration of the solutions was the same as that obtained in the neutralization measurements, and the temperature of observation was 20°:

TABLE XIII.

Solvent	Spec. conductivity.
Water	1.427
Acetone	0.0005626
Chloroform	0.0001036
Carbon tetrachloride	0.00003338
Ethyl acetate	0.00001844
Benzene	0.00001210

The aqueous solution conducts well and the acetone fairly well. In the former the heat evolved is approximately one-third the heat evolved when no solvent is used, while in the latter the heat evolved with and without the solvent is about equal. If a low value for the heat of neutralization signifies electrolytic dissociation, then the acetone in chloroform should be highly dissociated and should conduct well, but it does not. If the considerable evolution of heat obtained in the solution of pyridine acetate in water is assumed to be largely due to electrolytic dissociation of the acetate, we must at the same time assume a large negative heat of dissociation when the acetate is dissolved in acetone, where a conducting solution is also obtained. This assumption of a positive heat of electrolytic dissociation of a substance in one solvent and a negative heat of electrolytic dissociation in another is hardly justifiable.

As to the completeness of the reaction between pyridine and acetic acid in the different solvents, it can be said that there are a number of indications that the reaction is complete. In the first place, pyridine is a fairly strong base. Also, it has been found that salts of organic bases of ring series are, in general, "hydrolyzed" (*i. e.*, split apart in solution) to but a very slight extent.

Reactions in solution which are not complete reach the point of equilibrium but slowly, as a rule. With all of the solvents here used, however, it was always observed that the final temperature was attained very quickly indeed—as fast as the thermometer could acquire the new temperature. In fact the final temperature was attained just as quickly when pyridine and acetic acid were used in the various solvents as when hydrochloric acid and sodium hydroxide reacted with each other in aqueous solution. The considerable evolution of heat and the promptness with which the heat is liberated would argue for the completeness of the reaction.

Unfortunately we have not many methods for determining the state of substances in solution, and of those which we have but few are applicable to the case in hand. The boiling point of pyridine acetate is too near

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that of the solvents to make the ebullioscopic method applicable, and the cryoscopic method is available for but two of the solvents used, *viz.*, water and benzene. Measurements of the molecular weight of pyridine acetate in these two solvents were accordingly made by this method, the results of which appear in the accompanying table:

TABLE XIV.

MOLECULAR WEIGHT OF PYRIDINE ACETATE IN BENZENE.

(By depression of the freezing point.)

Weight of solvent. Grams.	Weight of solute. Grams.	Depression of F. P.	Molecular weight.
20.56	0.9010	1.652°	132.5
20.56	1.7634	3.635°	140.0
20.56	2.3574	4.159°	137.8
20.56	2.7497	4.751°	140.7
Average.....			137.8

TABLE XV.

MOLECULAR WEIGHT OF PYRIDINE ACETATE IN WATER AND THE "DEGREE OF DISSOCIATION" CALCULATED THEREFROM.

(By depression of the freezing point.)

Weight of solvent. Grams.	Weight of solute. Grams.	Depression.	Molecular weight.	"Dissociation." Per cent.
25.85	0.5330	0.537°	71.42	94.8
25.85	1.0589	1.033°	73.76	88.5
19.73	1.5618	1.956°	75.27	84.7
19.73	2.4919	3.095°	75.90	83.3

It will be noted that in benzene solutions pyridine acetate showed a normal molecular weight—approximately 139—and that the individual determinations vary no more than do corresponding measurements of the molecular weight of such substances as sugar in water. Evidently pyridine acetate in benzene solutions is not split apart into its constituents but is a stable substance, and therefore the reaction between pyridine and acetic acid in benzene solutions may be considered as going to completion. While similar measurements are impossible in the case of acetone, ethyl acetate, chloroform, and carbon tetrachloride, it seems safe to conclude that in these cases also the reaction is complete, for they are substances which do not react with pyridine acetate nor with the base or acid composing it.

Where water is the solvent, the values for the molecular weight of pyridine acetate, in dilute solution, are approximately one-half the normal molecular weight, just as when any ordinary bivalent salt is used for such measurements in aqueous solution, and where, accordingly, a dissociation of the salt is assumed. The so-called degree of dissociation was calculated from the molecular weight determinations, and was found to decrease in a regular manner with increasing concentration, as it does

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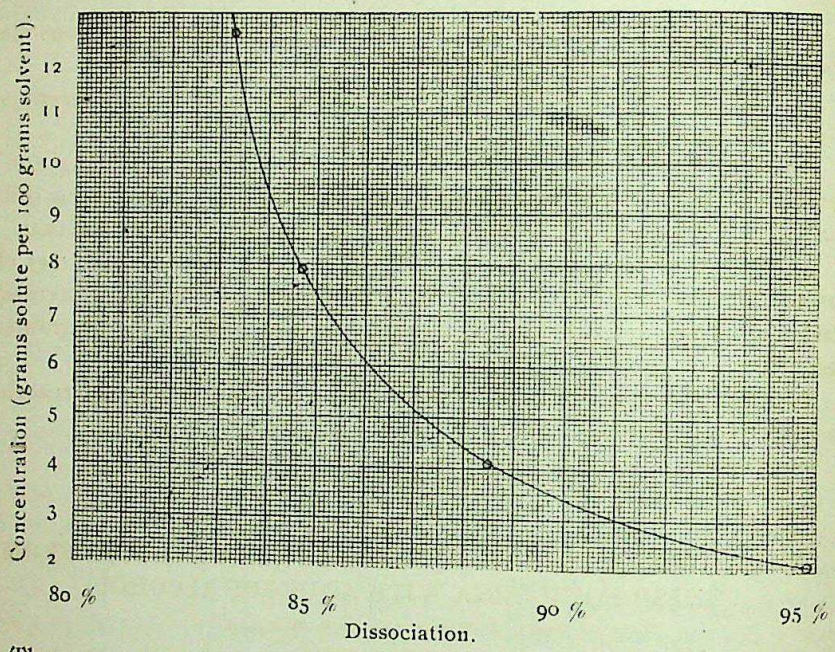
ordinarily. For the very dilute solutions the dissociation was practically complete. The change with concentration is shown in the accompanying graph:



These measurements tend to show that the condition in solution is what should be expected in case the reaction is complete.

Attempts were also made to measure the degree of dissociation of pyridine acetate in aqueous solution at 0° by the conductivity method, but this was found to be impracticable, as the values for the molecular (or equivalent) conductivity continually increased with dilution without ever attaining a maximum value, although the dilution was carried out to over a million liters. Similar difficulties are encountered with many other acetates, as is well known.

If we consider that neutralization is a process which includes only the acid and the base, then the differences in the final values for the heats of neutralization in different solvents are undoubtedly to be explained by the difference in the tenacity with which the reacting pyridine and acetic acid are held by the solvents in question. It is evident that the energy required to separate them from the solvent must be considerable in some cases.

If, on the other hand, the solutions of acid or of base in the particular solvent in question be considered as a new chemical complex, *i. e.*, a new chemical substance not following the law of definit proportions,[1] but

[1] Kahlenberg, *Science*, 31, 41 (1910).

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with definit acidic and basic properties, it is not at all strange that the heat of neutralization should vary considerably from solvent to solvent.

Summary.

1. Measurements of heats of reaction in non-aqueous solutions have been made and reported for the first time.

2. The amount of heat liberated for a given reaction in different solvents has been found to vary greatly from solvent to solvent.

3. These considerable differences cannot be explained as being due to any electrolytic dissociation of the acetate, nor are they due to differences in the heats of solution of the acetate in the different solvents.

4. The chemical nature of the solvents does not seem to give any clue as to the magnitude of the heat of neutralization in the cases investigated, nor of the magnitude or sign of the heat of solution of the resulting acetate.

It is proposed to continue this line of work, using such other reactions as may be found available.

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THE VAPOR PRESSURE OF HYDRATES, DETERMINED FROM THEIR EQUILIBRIA WITH AQUEOUS ALCOHOL.

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The measurement of the small pressures of dissociation common to hydrated salts is a problem that presents many difficulties and has been the subject of numerous researches. The most general plan has been to place the salt in the Torricellian vacuum, and measure the depression of the mercury of the barometric column. On this plan were the methods of Debray,[1] Wiedemann,[2] Pareau,[3] Lescoeur,[4] and others, using various means for complete removal of the air from the barometric space. Lescoeur[4] also devised a method for measuring these pressures by getting the dew-point of the atmosphere which was in equilibrium with the salt in a closed space, and the vapor pressure of water at that dew-point gave the required pressure. Müller-Erzbach,[5] who has contributed a great deal of work on this subject, attacked the problem in two ways: One way, which he afterwards abandoned, was by comparing the losses of water from tubes containing water and the hydrate respectively, when placed for a time over concentrated sulfuric acid. This gave him the

[1] *Compt. rend.*, 64, 603 (1867).
[2] *Pogg. Ann., Jubeband*, 474 (1873).
[3] *Wied. Ann.*, I, 55 (1877).
[4] *Ann. chim phys.*, [6] 16, 378 (1889).
[5] *Ber.*, 14, 1093 (1881); *Z. physik. Chem.*, 2, 113 (1888).

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relative rate of evaporation, which he took as equal to the relative pressure. His other plan was to find the dilution of sulfuric acid, over which the hydrate would neither gain nor lose weight. The vapor pressures of liquid and hydrate were therefore equal, and since that of the dilute acid had been measured by Regnault, the vapor pressure of the hydrate could be found from his tables. The most reliable data are probably those obtained by Frowein.[1] He arranged an apparatus in which the water vapor from the hydrates exerted a pressure on one side of a column of oil contained in a specially constructed U-tube, while sulfuric acid, contained in an expansion of the U-tube, kept the pressure of water vapor at zero on the other side. Means were devised for complete evacuation of the apparatus. Tammann[2] tried to measure these vapor pressures by passing dry air over the hydrates, and finding the weight of water taken up by a given volume of air. His results were not satisfactory. We have tried a similar plan, without success. The only other research on this subject that we have found, differing essentially from those already mentioned, was that of Linebarger.[3] He determined the equilibrium between hydrates and moist ether at the boiling temperature, then found the water content of the ether by a determination of its boiling point. A calculation of the partial pressure of the water vapor in the vapor from the ether solution gave him the vapor pressure of the hydrate. The theoretical basis of his work is the same as that upon which we have worked, and will now be discussed.

A pure hydrate may be in equilibrium at a given temperature with various pressures of water vapor, ranging between maximum and minimum limits. These limits are fixed as the vapor pressure of mixtures of the hydrate and the next higher hydrate of the salt (or its saturated solution) as a maximum, and the vapor pressure of mixtures of the hydrate and the next lower hydrate of the salt (or the anhydrous salt) as a minimum. This minimum pressure is the pressure usually meant in referring to the vapor pressure of a hydrate, and this meaning of the term will be understood in this paper. It follows from the above that a pure hydrate can be in equilibrium with various solutions of water and alcohol, whose aqueous pressures will lie between the maximum and minimum pressures of the hydrate itself. But a mixture of two hydrates can be in equilibrium with only one solution of water and alcohol, whose aqueous pressure must be equal to that of the mixture of hydrates.[4]

We have found the concentration of the alcohol-water solution in equilibrium at 25° with each of a number of hydrated salts, and have found the

[1] *Z. physik. Chem.*, 1, 5, 362 (1887).
[2] *Wied. Ann.*, 33, 322 (1888).
[3] *Z. physik. Chem.*, 13, 500 (1894).
[4] Nernst, "Theoretische Chemie" (6 Aufl.), p. 661.

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partial pressure of water in the vapor of this solution in each case. This partial pressure is equal to the vapor pressure of the hydrate.

EXPERIMENTAL WORK AND RESULTS.

(a) The Equilibrium between Hydrates and Aqueous Alcohol.

The salts used were obtained by recrystallizing the purest commercial salts available. Only those salts were chosen which were practically insoluble in alcohol. The crystals were filtered on a Büchner funnel, pressed between sheets of filter paper until free from excess water, and bottled. When a lower hydrate or the anhydrous salt was required, it was obtained by careful heating of the above material, until analysis showed the desired precentage of water, or a closed tube test showed no moisture whatever, as the case might be.

The sample of salt to be used for a determination was ground in a mortar and passed through a 100-mesh sieve—in some cases it was necessary to use a 200-mesh sieve—in order to get salt fine enough for a fairly rapid reaction. The first experiments were made without this precaution, using simply a mixture of powdered and crushed crystals, but the results were misleading. They could be explained only by assuming that the larger, solid crystals had resisted any change in water-content and equilibrium had not been reached. Water was determined in the sifted salt by ignition.

The alcohol was prepared by redistilling Kahlbaum's absolute alcohol with sodium, the first and last portions of the distillate being rejected. The resulting liquid was found by its specific gravity to be 99.8 per cent. alcohol.[1] From this absolute alcohol, mixtures were made of any desired composition, by adding distilled water from a buret to weighed amounts of alcohol. The exact composition of the mixture was then found from its specific gravity. Specific gravity determinations were made with an Ostwald pycnometer, holding approximately ten grams of water. This instrument was calibrated and used at 20°, and values for the specific gravities of alcohol-water solutions at that temperature were found by re-calculation from values given in Landolt and Börnstein's "Tabellen."

Experiments with hydrates and aqueous alcohol were carried out as follows: A portion of several grams of the sifted salt, weighed to a decigram, was put into a small bottle with a ground glass stopper. The alcohol was added from a calibrated pipette, usually 25 cc. for each experiment. The stopper was then tightly inserted, and the bottle-neck immersed in melted paraffin for an instant, leaving a coating of paraffin which was an effective seal. The bottle was then fastened to one of the arms of the rotating axis in a thermostat tank, and shaken at 25° for at least two days. When it was judged that equilibrium had been reached as nearly as possible, the bottles were removed, wiped dry, and carefully

[1] In Tables III, IV and V, this alcohol is tabulated as 100 per cent.

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opened. The liquid was then immediately filtered through a dry quantitative filter into a dry bottle. For alcohol containing but little water, this was done under a bell-jar, to avoid either evaporation or absorption of atmospheric moisture. The specific gravity of the clear liquid was taken, which gave its composition within 0.1 per cent. The salt was removed from the filter, and a gram or so of it pressed dry between filter papers as rapidly as possible, until no more odor of alcohol could be detected. Water was then determined by ignition. It was found, however, that results too high in water were obtained in this way, because of the more rapid evaporation of the alcohol than of the water from the solution with which the salt had been mixed; this left some water which would be rapidly taken up by the salt, especially if it were one poor in water. Therefore when the quantity of salt exceeded two grams, and the alcohol changed less than two per cent., more accurate results on the composition of the residue could be obtained by calculation from the alcohol data and the original composition of the salt.

The charges of salt and aqueous alcohol put into the bottles in these equilibrium experiments were planned according to the known properties of the hydrate concerned. Preliminary trials were often necessary to determine approximately the dilution of alcohol in equilibrium with the salts. Owing to the slowness of reaction, if too great a change was necessary before the system could come to equilibrium, this could not be reached in a reasonable time; hence, for the final data, changes of only one or two per cent. in the alcohol composition were provided for. In the case of the salts commonly used as drying agents, it was usually safe to assume that the lowest hydrates could be treated with absolute alcohol and be expected to come into equilibrium within one per cent. Then, some of the anhydrous salt could be mixed with about 98 per cent. alcohol and be expected to produce approximately the same composition of alcohol by dehydration as that obtained from absolute alcohol by hydration. The higher hydrates offered a more difficult problem, and a number of trial charges were often necessary, a guess at the equilibrium being all that was available at the outset. A mixture of two hydrates would be added to a known dilution of alcohol, thus providing for a change in either direction—removal or addition of water, raising or lowering the concentration of alcohol. If the result showed the former, the next experiment employed a higher percentage of alcohol; if the latter, a lower percentage. In tabulating the results, most of these preliminary trials have not been given, since they would add nothing to an understanding of the results.

The slowness of reaction when equilibrium was nearly reached made it difficult to obtain this point exactly, but the final error involved is small. This is true because the partial pressure of water in the vapor

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TABLE I.

Grams.	Salt used. Formula.	Alcohol used. Per cent.	Salt produced. Formula.	Alcohol at equilibrium. Per cent.	Solid phases at equilibrium.
5.0	K_2CO_3	98.2	$K_2CO_3.0.3H_2O$	99.20[2]	K_2CO_3 and $2K_2CO_3.3H_2O$
5.0	K_2CO_3	98.2	$K_2CO_3.0.3H_2O$	99.20	K_2CO_3 and $2K_2CO_3.3H_2O$
6.5	$K_2CO_3.1.5H_2O$	99.8	$K_2CO_3.1.2H_2O$	99.34	K_2CO_3 and $2K_2CO_3.3H_2O$
4.1	$K_2CO_3.1.5H_2O$	99.8	$K_2CO_3.1.3H_2O$	99.37	K_2CO_3 and $2K_2CO_3.3H_2O$
5.0	$K_2CO_3.1.4H_2O$	92.6	$K_2CO_3.1.5H_2O$	92.70	$2K_2CO_3.3H_2O$
1.8	K_2CO_3	90.2	$K_2CO_3.1.5H_2O$	91.30	$2K_2CO_3.3H_2O$
20.0	$Na_2SO_4.0.1H_2O$	50.7[1]	$Na_2SO_4.0.14H_2O$	52.7[2]	Na_2SO_4 and $Na_2SO_4.10H_2O$
30.0	$Na_2SO_4.0.2H_2O$	55.2[1]	$Na_2SO_4.0.15H_2O$	52.6	Na_2SO_4 and $Na_2SO_4.10H_2O$
10.0	$Na_2SO_4.10H_2O$	60.0	$Na_2SO_4.2.7H_2O$	53.5	Na_2SO_4 and $Na_2SO_4.10H_2O$
15.0	Na_2SO_4	50.7	$Na_2SO_4.1.8H_2O$	53.3	Na_2SO_4 and $Na_2SO_4.10H_2O$
15.0	$Na_2SO_4.10H_2O$	54.2[1]	$Na_2SO_4.9.4H_2O$	52.6	Na_2SO_4 and $Na_2SO_4.10H_2O$
2.5	CaO	98.0	$CaO.0.3H_2O$	99.37	CaO and $Ca(OH)_2$
2.5	CaO	98.0	$CaO.0.25H_2O$	99.13	CaO and $Ca(OH)_2$
6.0	$CaO.0.7H_2O$	99.8	$CaO.0.6H_2O$	99.50	CaO and $Ca(OH)_2$
6.0	$CaO.0.7H_2O$	99.8	$CaO.0.7H_2O$	99.8	CaO and $Ca(OH)_2$
10.0	$MgSO_4.0.7H_2O$	99.8[1]	$MgSO_4.0.6H_2O$	99.57	$MgSO_4$ and $MgSO_4.H_2O$
10.0	$MgSO_4.0.7H_2O$	99.8	$MgSO_4.0.6H_2O$	99.70	$MgSO_4$ and $MgSO_4.H_2O$
6.0	$MgSO_4$	98.0	$MgSO_4.0.4H_2O$	99.13	$MgSO_4$ and $MgSO_4.H_2O$
6.0	$MgSO_4$	98.0	$MgSO_4.0.4H_2O$	99.17	$MgSO_4$ and $MgSO_4.H_2O$
7.0	$MgSO_4.1.2H_2O$	91.8	$MgSO_4.2.2H_2O$	96.2	$MgSO_4.H_2O$ and $MgSO_4.4H_2O$
7.0	$MgSO_4.3.6H_2O$	99.8	$MgSO_4.2.0H_2O$	98.1	$MgSO_4.H_2O$ and $MgSO_4.4H_2O$
5.0	$MgSO_4.3.6H_2O$	96.2	$MgSO_4.3.6H_2O$	96.2	$MgSO_4.H_2O$ and $MgSO_4.4H_2O$

[1] Corrected for a small amount of dissolved salt, found by evaporating the liquid from the pycnometer.
[2] 30 cc. of alcohol.

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TABLE I (*Continued*).

Grams.	Salt used. Formula.	Alcohol used. Per cent.	Salt produced. Formula.	Alcohol at equilibrium. Per cent.	Solid phases at equilibrium.
7.0	$MgSO_4.4.2H_2O$	91.6	$MgSO_4.4.05H_2O$	91.0	$MgSO_4.4H_2O$ and $MgSO_4.5H_2O$
4.0	$MgSO_4.4.2H_2O$	88.3	$MgSO_4.5.0H_2O$	90.2	$MgSO_4.4H_2O$ and $MgSO_4.5H_2O$
3.0	$MgSO_4.6.2H_2O$	90.6	$MgSO_4.5.9H_2O$	90.1	$MgSO_4.5H_2O$ and $MgSO_4.6H_2O$
7.0	$MgSO_4.6.2H_2O$	91.8	$MgSO_4.5.5H_2O$	89.2	$MgSO_4.5H_2O$ and $MgSO_4.6H_2O$
4.0	$MgSO_4.5.6H_2O$	88.3	$MgSO_4.5.9H_2O$	88.8	$MgSO_4.5H_2O$ and $MgSO_4.6H_2O$
7.5	$MgSO_4.7H_2O$	87.8	$MgSO_4.6.8H_2O$	87.3	$MgSO_4.6H_2O$ and $MgSO_4.7H_2O$
7.5	$MgSO_4.6H_2O$	84.5	$MgSO_4.6.4H_2O$	85.9	$MgSO_4.6H_2O$ and $MgSO_4.7H_2O$
8.0	$MgSO_4.6.9H_2O$	86.7	$MgSO_4.6.95H_2O$	86.9	$MgSO_4.6H_2O$ and $MgSO_4.7H_2O$
6.0	$ZnSO_4.H_2O$	99.8	$ZnSO_4.0.9H_2O$	99.5	$ZnSO_4$ and $ZnSO_4.H_2O$
5.0	$ZnSO_4.H_2O$	99.8	$ZnSO_4.0.8H_2O$	99.4	$ZnSO_4$ and $ZnSO_4.H_2O$
4.0	$ZnSO_4$	98.8	$ZnSO_4.0.3H_2O$	99.3	$ZnSO_4$ and $ZnSO_4.H_2O$
7.0	$ZnSO_4.1.2H_2O$	83.0	$ZnSO_4.1.2H_2O$	83.0	$ZnSO_4.H_2O$ and $ZnSO_4.6H_2O$
5.0	$ZnSO_4.H_2O$	81.8	$ZnSO_4.1.4H_2O$	82.5	$ZnSO_4.H_2O$ and $ZnSO_4.6H_2O$
5.1	$ZnSO_4.6.2H_2O$	84.1	$ZnSO_4.6.0H_2O$	83.8	$ZnSO_4.H_2O$ and $ZnSO_4.6H_2O$
9.0	$ZnSO_4.6.5H_2O$	80.8	$ZnSO_4.6.3H_2O$	80.3	$ZnSO_4.6H_2O$ and $ZnSO_4.7H_2O$
4.6	$ZnSO_4.6.2H_2O$	79.2	$ZnSO_4.6.3H_2O$	79.4	$ZnSO_4.6H_2O$ and $ZnSO_4.7H_2O$
6.7	$CuSO_4$	98.0[1]	$CuSO_4.0.5H_2O$	99.53	$CuSO_4$ and $CuSO_4.H_2O$
6.7	$CuSO_4$	98.0[1]	$CuSO_4.0.5H_2O$	99.37	$CuSO_4$ and $CuSO_4.H_2O$
3.5	$CuSO_4.H_2O$	99.8	$CuSO_4.0.8H_2O$	99.63	$CuSO_4$ and $CuSO_4.H_2O$
3.5	$CuSO_4.H_2O$	99.8	$CuSO_4.0.8H_2O$	99.60	$CuSO_4$ and $CuSO_4.H_2O$

[1] 30 cc. alcohol.

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8.0	$CuSO_4.2.5H_2O$	97.0	$CuSO_4.2.0H_2O$	96.6	$CuSO_4.H_2O$ and $CuSO_4.3H_2O$
4.0	$CuSO_4.H_2O$	95.0	$CuSO_4.1.7H_2O$	96.0	$CuSO_4.H_2O$ and $CuSO_4.3H_2O$
8.0	$CuSO_4.2.5H_2O$	97.1	$CuSO_4.2.4H_2O$	96.4	$CuSO_4.H_2O$ and $CuSO_4.3H_2O$
3.8	$CuSO_4.H_2O$	95.0	$CuSO_4.2.0H_2O$	96.2	$CuSO_4.H_2O$ and $CuSO_4.3H_2O$
5.0	$CuSO_4.H_2O$	95.1	$CuSO_4.1.7H_2O$	96.2	$CuSO_4.H_2O$ and $CuSO_4.3H_2O$
5.0	$CuSO_4.4\ H_2O$	99.8	$CuSO_4.2.7H_2O$	96.8	$CuSO_4.H_2O$ ane $CuSO_4.3H_2O$
5.0	$CuSO_4.4.0H_2O$	94.2	$CuSO_4.3.8H_2O$	93.7	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
4.9	$CuSO_4.H_2O$	87.2	$CuSO_4.4.2H_2O$	93.2	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
8.0	$CuSO_4.H_2O$	87.2	$CuSO_4.2.8H_2O$	93.3	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
2.0	$CuSO_4.1.8H_2O$	92.6	$CuSO_4.3.8H_2O$	93.6	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
5.0	$CuSO_4.2.8H_2O$	92.9	$CuSO_4.3.7H_2O$	93.5	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
2.0	$CuSO_4.5H_2O$	94.8	$CuSO_4.4.7H_2O$	94.1	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
5.0	$BaCl_2.2H_2O$	99.0	$BaCl_2.1.4H_2O$	96.7	$BaCl_2.H_2O$ and $BaCl_2.2H_2O$
9.2	$BaCl_2.1.6H_2O$	93.5	$BaCl_2.1.8H_2O$	95.0	$BaCl_2.H_2O$ and $BaCl_2.2H_2O$
5.9	$BaCl_2.0.8H_2O$	95.0	$BaCl_2.1.8H_2O$	96.3	$BaCl_2.H_2O$ and $BaCl_2.2H_2O$
8.0	$BaCl_2.1.8H_2O$	96.0	$BaCl_2.1.9H_2O$	96.3	$BaCl_2.H_2O$ and $BaCl_2.2H_2O$
6.9	$BaCl_2.0.4H_2O$	98.0[1]	$BaCl_2.0.6H_2O$	98.4	$BaCl_2$ and $BaCl_2.H_2O$
5.0	$BaCl_2.0.4H_2O$	98.0[1]	$BaCl_2.0.5H_2O$	98.1	$BaCl_2$ and $BaCl_2.H_2O$
5.0	$Na_2HPO_4.10.2H_2O$	54.0	$Na_2HPO_4.11.0H_2O$	54.4	$Na_2HPO_4.7H_2O$ and $Na_2HPO_4.12H_2O$
7.0	$Na_2HPO_4.8.9H_2O$	57.6	$Na_2HPO_4.7.9H_2O$	55.7	$Na_2HPO_4.7H_2O$ and $Na_2HPO_4.12H_2O$
6.0	$Na_2HPO_4.7.1H_2O$	54.6	$Na_2HPO_4.7.0H_2O$	54.3	$Na_2HPO_4.7H_2O$ and $Na_2HPO_4.12H_2O$
7.0	Na_2HPO_4	76.0	$Na_2HPO_4.2.5H_2O$	83.2	$Na_2HPO_4.2H_2O$ and $Na_2HPO_4.7H_2O$
5.0	$Na_2HPO_4.6.5H_2O$	85.4	$Na_2HPO_4.5.5H_2O$	84.2	$Na_2HPO_4.2H_2O$ and $Na_2HPO_4.7H_2O$
4.0	$Na_2HPO_4.1.9H_2O$	90.2	$Na_2HPO_4.2.0H_2O$	90.3	Na_2HPO_4 and $Na_2HPO_4.2H_2O$
6.0	$Na_2HPO_4.2.0H_2O$	90.6	$Na_2HPO_4.1.9H_2O$	90.5	Na_2HPO_4 and $Na_2HPO_4.2H_2O$

[1] 50 cc. alcohol.

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of the alcohol solution changes, on the average, only 0.24 mm. for a change of one per cent. on the alcohol content. This change is not a linear function of the composition, but at most never exceeds 1.0 mm. for each difference of one per cent. in the molecular composition of the liquid. Hence, if the alcohol solution in equilibrium with the hydrate is located within one per cent., the value calculated for the vapor pressure of the hydrate will be fairly accurate—probably fully as accurate as most of the data on vapor pressures of hydrates found in the literature.

The results for the salts investigated are tabulated above. Formulas showing fractional molecular proportions of water are used for convenience in indicating composition. The quantity of alcohol in each charge is 25 cc., except where otherwise noted.

The results on potassium carbonate show that the hydrate $2K_2CO_3.3H_2O$ has a minimum vapor pressure equal to that of the water in 99.3 per cent. alcohol. That this hydrate is the one which forms from water solution at 25° was shown by recrystallizing some of the salt in a flask suspended in the thermostat, then analyzing some of the crystals. Before analysis, the crystals were freed from surplus water by standing over sulfuric acid—since this salt deliquesces in ordinary air. They were removed before any sign of efflorescence appeared, and ignited to determine water. A sample was boiled with tenth-normal hydrochloric acid, the excess of acid titrated with tenth-normal alkali, and K_2CO_3 calculated:

	Found.	Theory for $2K_2CO_3.3H_2O$.
H_2O	16.66	16.34
K_2CO_3	83.18	83.66
	99.84	100.00

This work is mentioned because there seems to be some uncertainty in the reference books as to the hydrate of this salt.

Sodium sulfate evidently has only one hydrate, the decahydrate, stable at 25°, and this has a vapor pressure measured by the aqueous pressure of 53.0 per cent. alcohol. This conclusion is sustained by the work of Schreinemakers[1] on solution equilibrium, who found a similar dilution of alcohol in equilibrium with the decahydrate.

It was difficult to reach equilibrium with lime, especially in attempts to hydrate absolute alcohol, using the hydroxide. The results are not contradictory, however, and show that lime is an excellent drying agent, producing approximately 99.5 per cent. alcohol.

Equilibrium was reached very slowly with magnesium sulfate. Several hydrates may be distinguished here. The same remarks apply to zinc sulfate. Copper sulfate was worked out rather carefully, because of the frequent use of this salt as a text-book illustration of the peculiari-

[1] *Z. physik. Chem.*, **67**, 551 (1909).

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ties in vapor pressures of hydrates. The two hydrates of barium chloride have rather low vapor pressures. Sodium phosphate has an efflorescent hydrate, like that of sodium sulfate, and shows a corresponding equilibrium for the mixtures of the two higher hydrates, with 54.4 per cent. alcohol. This work demonstrates the existence of a dihydrate, about which there appears to be no certainty in the literature.

(b) The Composition of the Vapors from Aqueous Alcohol.

In order to find the pressure of water vapor in equilibrium with a given dilution of alcohol, it was necessary first to know the relative proportion of alcohol and water molecules in the vapor. This furnished by calculation a number representing the average molecular weight of the vapor, and this was later used in finding the total pressure. Then from the total pressure of a mixture, using as a factor the molecular per cent. of water in its vapor, the partial pressure of water vapor for the mixture could be calculated.

The means employed in determining the composition of these vapors consisted in analyzing them by combustion. Linebarger[1] has determined the composition of the vapors from mixed liquids, in which one component was an acid, or contained sulfur or a halogen, by a somewhat similar method. The general plan of the present work was to carry the vapors from the alcohol at 25° by means of a stream of pure, dry air, into a combustion furnace, the products of combustion and the original water of the vapor being collected and weighed in suitable apparatus, and the original constituents of the vapors determined by calculation from the analytical data.

The apparatus for this work was arranged as follows: Air under pressure, controlled by a valve so that the flow was about 50–60 cc. per minute, was led through a purifying apparatus. This comprised a wash-bottle containing a fifty per cent. solution of caustic potash, a tower filled with sticks of dry potash, and finally a wash-bottle containing concentrated sulfuric acid. From this apparatus the air passed into a Y-tube, the left-hand arm of which led through a series of two Geissler potash bulbs containing the aqueous alcohol, then into a second Y-tube inserted through a rubber stopper in the combustion tube of the furnace. A by-pass, closed by pinchcocks, connected the right-hand arms of the two Y-tubes. The combustion tube was filled with cupric oxide. Exit from this was through a series of three Geissler potash bulbs. The first contained concentrated sulfuric acid; the second, a fifty per cent. solution of caustic potash; the third, sulfuric acid like the first, to catch water vapor from the potash solution. This arrangement of absorption bulbs was adopted only after some preliminary work had shown that it was decidedly better than the arrangement commonly used in combustions.

[1] This Journal, 17, 615 (1895).

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A preliminary set of experiments on combustion of alcohol vapors were carried out by Mr. H. H. Guest, of this laboratory, previous to the work here described. Many of the difficulties of the process were found out and provided against by him.

When a determination was to be made, the alcohol bulbs were filled with fresh alcohol of known specific gravity, and connected in place by means of short, thick pieces of rubber tubing, so arranged that the ends of the glass tubes in all cases came together. The bulbs were supported in a tank of water which was maintained at 25° and stirred. The furnace had previously been heated to redness, and the pieces of absorption apparatus attached. These had been separately weighed against a counterpoising bulb of the same form. The air was now turned on through the alcohol bulbs, and the combustion continued for about one hour. The amount of vapor that could be successfully burned was of course limited by the capacity for carbon dioxide of the potash in the absorption bulb. The rule was to stop when half the theoretical amount had been produced and absorbed, as could be judged from earlier experiments. The tubes leading from the air-purifying apparatus through the alcohol bulbs were now closed by screw pinchcocks, and the by-pass opened. By this means the furnace was swept clean of the products of combustion, a process for which fifteen minutes were allowed. The absorption bulbs were detached and weighed as usual, the gain of the first bulb representing water, that of the other two carbon dioxide. The weights of alcohol and water, respectively, in the vapor were found by calculation from the weights of carbon dioxide and water and their chemical relations to alcohol. The molecular per cent. of water in the vapor could then be calculated.

TABLE II.

Actual per cent. alcohol in liquid.	Molecular per cent. water in liquid.	Molecular per cent. water found in vapor.				
		I.	II.	III.	IV.	Average of I–IV.
96.35	8.66	5.85	6.11	4.44	5.73	5.53
95.60	10.53	8.48	.....	.....	.....	8.48
95.20	11.42	10.58	10.00	.....	.....	10.29
93.51	15.09	12.13	12.01	12.56	11.48	12.04
89.00	24.00	17.22	17.19	16.76	.....	17.06
84.17	32.58	23.24	22.78	22.22	.....	22.74
69.04	53.45	31.14	29.49	30.93	.....	30.52
53.77	68.79	36.36	36.99	36.91	.....	36.75
39.33	79.73	40.71	39.65	.....	.....	40.18
29.97	85.66	45.06	44.82	.....	.....	44.94
20.34	90.89	57.25	56.06	.....	.....	56.66
9.50	96.05	73.74	73.36	.....	.....	73.55

The greatest care was exercised in these analyses, and the results are considered as accurate as it is practicable to obtain by this method;

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and we know of no other method which could be expected to give as satisfactory results. An error of one milligram in the weight of an absorption bulb produced in the case of some of the richer alcohol-water mixtures a difference of 0.5 per cent. in the molecular per cent. found, and it was hard to make the weights of carbon dioxide and water so large that this limit of accuracy was much exceeded. Even with the more dilute mixtures, an error of one milligram in weighing produced a difference of more than 0.2 per cent. in the final result. The preceding table gives the results of the combustions.

The above results are expressed graphically below, where the molecular per cent. of water in the liquid is plotted as abscissa, and the molecular per cent. of water in the vapor as ordinate, in a curve.

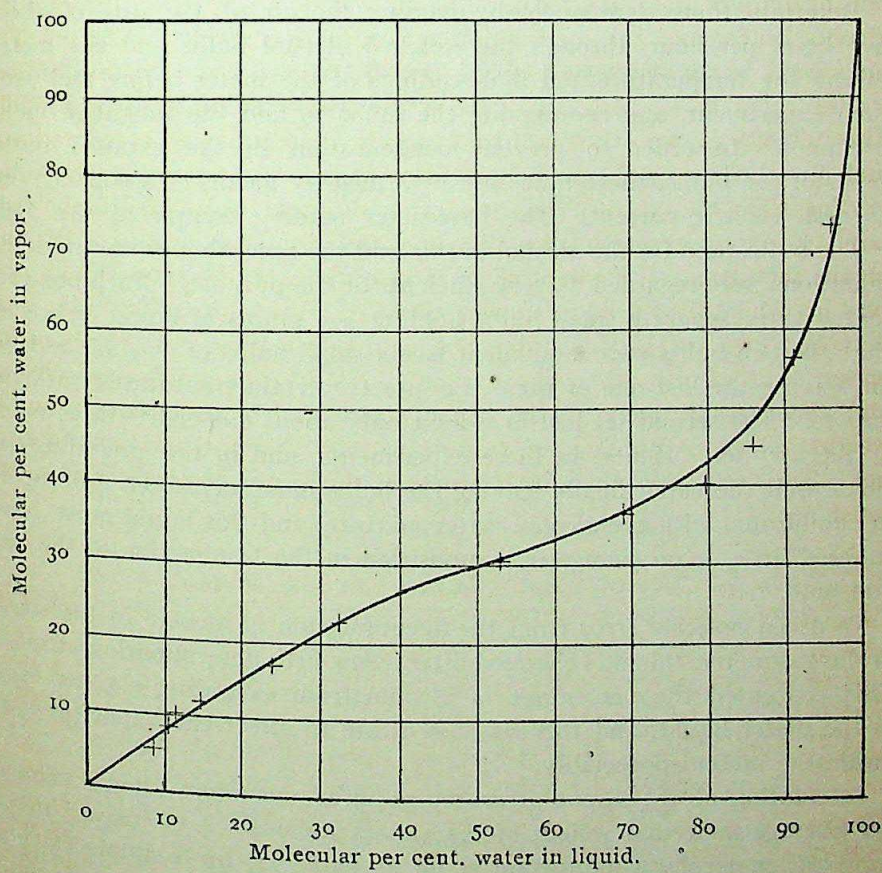

Fig. 1.

(c) The Vapor Pressures of Alcohol-Water Mixtures.

The method used to determin the total pressure of the vapors from aqueous alcohol depends on Dalton's law of partial pressures. It rests on the principle that if a given volume of air be saturated with a vapor,

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and if the weight of vapor, the molecular weight of the vaporized substance, and the corrected volume of air be known, the vapor pressure of the liquid from which the vapor was derived can be calculated. This principle was applied by Tammann[1] and Linebarger.[1]

The apparatus for the measurement in question was arranged as follows: The air was supplied and purified as in the preceding experiments, and the alcohol bulbs were similarly placed in a thermostat at 25.° No by-pass was necessary. The second alcohol bulb was connected directly with a wet gas meter, which had a drum capacity of 0.2 cu. ft., and read 0.001 cu. ft. on the dial. This meter had been proven at the laboratory of the New Haven Gas Co., and found accurate to 0.1 per cent. We are indebted to Dr. A. P. Beardsley for this assistance.

Determinations were made by passing the air at the rate of about five liters per hour, through the weighed alcohol bulbs and the meter, taking the temperature and dial-readings of the meter before and after each experiment, and re-weighing the bulbs to find the weight of vapor produced. In order to prevent condensation in the exposed outlet tubes of the bulbs, these tubes were warmed by means of a coil carrying a small electric current. The barometer reading completed the data.

The bulbs used for the alcohol in this and the preceding groups of determinations were regarded as very efficient for the purpose. Each one contained three separate small bulbs holding 4–5 grams of liquid apiece, so that the two bulbs were equivalent to six small bulbs of alcohol, and the air leaving the last one of these was pretty certainly saturated with the vapors. The second set lost in weight only about one-eightieth as much as the first set. Hence, in these experiments, and in the preceding series as well, the vapor finally leaving the bulbs must have been thoroughly in equilibrium with the alcohol-water mixture, and this liquid must have suffered little or no change in composition in the last section of the second bulb.

To avoid possible error from the accumulation of alcohol in the water in the gas meter, this was changed after every fifth determination at most. This prevented the percentage of alcohol from exceeding 0.5 per cent. in the meter liquid, and this was too dilute to affect the vapor pressure inside the meter appreciably.

Calculation of the vapor pressures required one more known value—the average molecular weight of the vapors themselves. This was found from the molecular composition given in Table II, by a simple calculation. The calculation of the vapor pressures was done by a formula similar to that given in Ostwald-Luther, "Physiko-Chemische Messungen," page 273. The air as registered by the meter is corrected in volume to standard conditions, $= v_0$. Given, that a gram-molecule of any gas

[1] *Loc. cit.*

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under standard conditions occupies 22.4 liters, then the volume that would be occupied by the mixed vapors without the air can be calculated, $= v_2$. The sum of these two corrected volumes is the volume that would be occupied by the air, saturated at 25° with the alcohol vapors, if it could be placed under standard conditions without losing the vapor. The volume of mixed vapors, divided by this sum, gives the partial pressure of the vapors, and this factor multiplied by 760 gives the pressure sought in millimeters of mercury $= p$, *i. e.*, if v is the volume in liters as read on the meter, p_1 the barometer reading, p_2 the vapor pressure of water at the meter temperature, P = 760. T = 273, t is the temperature of the meter, g is the weight of the vapors, and M their average molecular weight, then

$$\frac{v(p_1 - p_2)T}{760(T + t)} = v_0, \text{ and } \frac{22.4g}{M} = v_2, \text{ and } p = \frac{760v_2}{v_0 + v_2}$$

In Table III are given the results of the measurements of total vapor pressures of alcohol-water mixtures:

TABLE III.

Per cent. alcohol used.	M.[1]	Liters of air.	Temp. of meter.	Barometer reading. mm.	Grams of vapor.	Vapor pressure. mm.	Average vapor pressure.
100.00	46.05	5.664	21.0	758	0.9032	60.04	.....
100.00	46.05	5.896	21.5	763	0.9159	59.26	.....
100.00	46.05	5.638	17.5	769	1.3702	59.85	59.72
96.35	44.49	5.664	14.5	749	0.8644	58.53	.....
96.35	44.49	5.692	20.5	764	0.8574	58.26	.....
96.35	44.49	5.664	19.0	765	0.8519	57.78	58.19
93.51	42.68	5.678	19.5	766	0.8233	58.11	.....
93.51	42.68	5.721	18.5	761	0.8329	58.42	58.26
89.00	41.26	5.664	18.5	759	0.7833	57.62	.....
89.00	41.26	5.678	19.0	758	0.7810	57.51	57.57
84.17	39.67	5.947	18.5	760	0.7813	56.89	.....
84.17	39.67	5.664	19.5	760	0.7391	56.79	56.84
69.04	37.50	5.664	21.0	762	0.6539	53.63	.....
69.04	37.50	5.664	21.5	763	0.6406	52.68	.....
69.04	37.50	5.664	20.5	764	0.6517	53.18	53.17
53.77	36.75	5.664	21.0	764	0.5880	49.38	.....
53.77	36.75	5.664	21.0	764	0.5886	49.43	49.40
39.33	34.79	5.664	20.0	765	0.5321	47.06	.....
39.33	34.79	5.664	20.5	775	0.5292	46.37	46.71
29.97	33.45	8.496	21.5	773	0.6868	42.14	.....
29.97	33.45	11.328	21.0	763	0.9174	42.76	42.45
20.34	30.17	8.538	21.0	762	0.5528	38.20	.....
20.34	30.17	11.328	21.0	752	0.7324	38.62	38.41
9.50	25.43	11.328	21.0	749	0.4877	30.96	.....
9.50	25.43	11.328	21.0	749	0.4814	30.58	30.77
water	18.02	16.992	21.0	766	0.4059	23.52	.....
water	18.02	12.631	19.0	765	0.2995	23.57	23.54

[1] The average molecular weight of the vapor.

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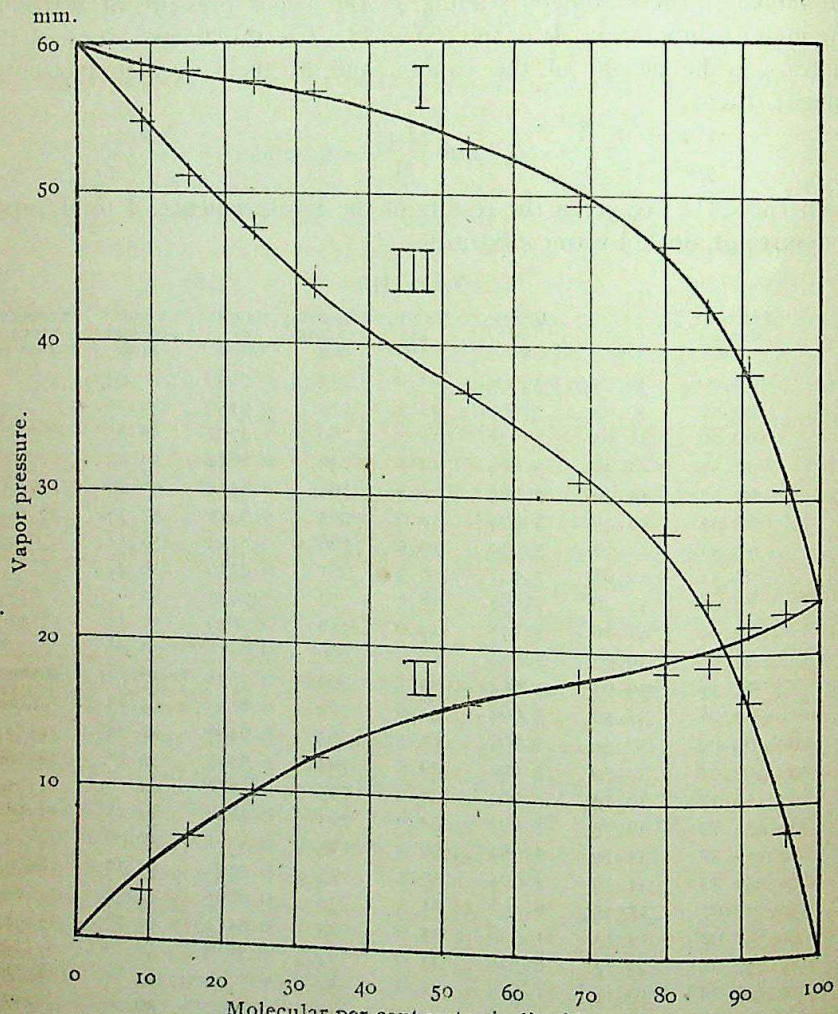
A set of values furnishing an interesting comparison with the results above were obtained by means of the formula of Doroszewsky and Polansky.[1] They determined the boiling points of various alcohol-water mixtures at pressures of 700, 760, and 800 mm., and found from their results that the absolute temperatures of the boiling points were proportional to the pressures. From this relation they obtained a formula for calculating the vapor pressure of a given mixture: if t_1 is the given temperature, t the boiling point of the given mixture at 760 mm., and x the



I. Total vapor pressure of alcohol—water mixtures.
II. Partial vapor pressure of water.
III. Partial vapor pressure of alcohol.

Fig. 2.

[1] *Z. physik. Chem.*, **73**, 192 (1910).

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boiling point of pure alcohol at the pressure required, $\frac{t + 273}{t_1 + 273} = \frac{78.3 + 273}{x + 273}$. The vapor pressure of pure alcohol at x is the pressure required. Using the boiling points of various dilutions of alcohol at 760 mm., given by Noyes and Warfel[1] and the vapor pressures of pure alcohol at certain temperatures given by Landolt and Börnstein,[2] we have calculated by this means vapor pressures for alcohol-water mixtures for which data are given in Table III, and these are arranged below for comparison:

TABLE IV.

Per cent. alcohol.	t.	Calculated vapor pressure.	Measured vapor pressure.
100.00	78.300	59.03	59.73
96.35	78.178	59.55	58.19
93.51	78.211	59.48	58.26
89.00	78.385	58.97	57.57
84.17	78.70	58.06	56.84
69.04	80.04	54.44	53.17
53.77	81.88	49.72	49.40
39.33	83.20	46.64	46.71
29.97	84.70	43.31	42.45
20.34	87.10	38.54	38.41
9.50	92.15	30.25	30.77

The agreement is good, considering the variety of data used and the fact that the formula can be regarded only as an approximation, for temperatures considerably removed from those at which it was derived.

In the next table, the results of the last two series of experiments are given, together with the partial pressures of water and alcohol derived from them:

TABLE V.

Liquid.		Vapor.			
Per cent. alcohol by weight.	Molecular per cent. water.	Molecular per cent. water.	Total Pressure. Mm.	Partial pressure, water.	Partial pressure, alcohol.
100.00	0.00	0.00	59.72	0.00	59.72
96.35	8.83	5.53	58.19	3.21	54.98
93.51	15.07	12.04	58.26	7.01	51.25
89.00	24.00	17.06	57.57	9.79	47.78
84.17	32.47	22.74	56.84	12.92	43.92
69.04	53.42	30.52	53.17	16.23	36.94
53.77	68.72	36.75	49.40	18.15	31.25
39.33	79.95	40.18	46.71	18.77	27.94
29.97	85.65	44.94	42.45	19.07	23.38
20.34	90.91	56.66	38.41	21.76	16.65
9.50	96.05	73.55	30.77	22.63	8.14
0.00	100.00	100.00	23.54	23.54	0.00

The values in the last three columns above are plotted as ordinates of

[1] THIS JOURNAL, 23, 463 (1901).
[2] "Tabellen" (3 Aufl.), p. 136.

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the curves on page 1322, with the values in the second column as abscissas. The forms of these curves show that the addition of a small amount of alcohol to water, or to a very dilute alcohol, causes a disproportionately large increase in vapor pressure. On the other hand, the addition of water to the higher concentrations of alcohol causes no great change in vapor pressure. At the ends of the curves, there are differences between the observed and smoothed-out valves, because of the difficulty in getting accurate results with mixtures high in either constituent.

Summary and Comparison of Results.

Taking from Curve II the values corresponding to the alcohol-water mixtures found to be in equilibrium with various hydrates, we have the vapor pressures of the latter. In the next table are incorporated the pressures so measured for the salts investigated, and, for the purpose of comparison, values determined by others. In this table, the formula representing a mixture of hydrates is placed in the first column; in the second column is the per cent. of alcohol in the mixture in equilibrium with the mixture of hydrates; in the third, the molecular per cent. of water in this liquid; and in the fourth, the calculated vapor pressure of the hydrate in millimeters of mercury. The last four columns contain the results of other measurements on hydrates. They are in most cases obtained for 25° by interpolation from the published figures. Our results are uniformly lower than Frowein's, but his values would be expected to have a positive error, if any, because of possible failure to remove all air from his apparatus. The same would be true of the work of Les-

Salt.	Per cent. alcohol.	Molecular per cent. water.	Vapor pressure.	Values found by			
				Frowein.	Lescoeur.	Pareau.	Müller-Erzbach.
$CuSO_4.3-5H_2O$	93.6	14.9	7.0	7.3	8.5	7.9	7.3
$CuSO_4.1-3H_2O$	96.5	8.7	4.7	....	....	...	4.6
$CuSO_3.0-1H_2O$	99.5	1.3	0.8	....	....	...	0.5
$Na_2SO_4.0-10H_2O$	53.0	69.4	18.2	....	19.0	...	17.6
$K_2CO_3.0-1.5H_2O$	99.3	1.7	1.1	....	1.5	...	....
$CaO.0-1H_2O$	99.5	1.3	0.8	....	....	...	....
$ZnSO_4.6-7H_2O$	79.9	39.1	13.6	14.6	14.0	...	12.9
$ZnSO_4.1-6H_2O$	83.0	34.4	12.8	13.2	....	...	11.7
$ZnSO_4.0-1H_2O$	99.4	1.5	1.0	....	....	...	0.5
$MgSO_4.6-7H_2O$	87.1	27.0	11.5	11.6	11.7	...	....
$MgSO_4.5-6H_2O$	89.0	23.9	9.8	....	....	...	....
$MgSO_4.4-5H_2O$	90.6	20.8	8.8	....	....	...	....
$MgSO_4.1-4H_2O$	96.2	9.0	4.9	....	....	...	....
$MgSO_4.0-1H_2O$	99.4	1.5	1.0	....	....	...	....
$BaCl_2.1-2H_2O$	96.3	8.9	4.8	5.2	....	2.9	4.7
$BaCl_2.0-1H_2O$	98.4	4.0	2.5	....	....	...	2.4
$Na_2HPO_4.7-12H_2O$	54.4	68.2	18.0	18.6	18.0	...	17.6
$Na_2HPO_4.2-7H_2O$	83.7	33.2	12.4	....	....	...	13.6
$Na_2HPO_4.0-2H_2O$	90.4	20.4	8.9	....	....	...	1.4

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coeur. Pareau must have been working with the lower hydrate of barium chloride, for which he finds the vapor pressure 2.9. Müller-Erzbach's results for vapor pressures are obtained by using his values for relative pressure at about 18° as factors with the vapor pressure of water at 25°, since, according to him, there is not much change in the relative pressure for a few degrees difference in temperature.

Application of Vapor Pressures in the Choice of Salts as Drying Agents.

It was one of the earliest chemical operations to free a liquid from water by using a salt. Lescoeur[1] says that Raymond Lully, in the XIIth Century, found that potassium carbonate would remove most of the water from alcohol. It is, of course, a very common practice to-day, in organic chemistry, to use salts that form hydrates for drying liquids. Only one research, however, and that a recent one, has been found which aims at studying the efficiency of the various salts used. In this, Siebenrock[2] shows that calcium chloride and potassium carbonate produce ether nearest free from water, while the much used sodium sulfate is really a poor drier; magnesium sulfate (forming the heptahydrate) is better.

In the present work, the percentage of alcohol found in equilibrium with the various salts shows directly their drying efficiency. It has been feasible to work this out for salts having only a small solubility in alcohol, and the chlorides of calcium and strontium have been omitted because of their solubility and the fact that they form alcoholates.

Two cases of liquids to be freed from water may be distinguished in this connection: one, of a liquid which dissolves water, either to a considerable extent or in all proportions; the other, of a liquid in which water is not appreciably miscible, but is present as an emulsion. When an anhydrous salt is added to a liquid of the first sort, containing water, equilibrium is established finally between the vapor pressure of the hydrate that forms and the partial pressure of water vapor from the mixed liquids in which it is. The salt chosen must have therefore a hydrate of low vapor pressure, and at the same time of high percentage of water. Calcium chloride answers these conditions well for liquids in which it is insoluble. Copper sulfate is excellent, but its lowest hydrate contains only about ten per cent. of water; potassium carbonate is in the same class, having about sixteen per cent. of water in its lowest hydrate; while the sulfates of magnesium and zinc, used in quantities such that only their monohydrates can form with the amount of water present, are very good driers. It is clear that sodium sulfate would be worthless here. For instance, water-alcohol mixtures are only dehydrated by it to the extent of 53.0 per cent. alcohol, as shown above.

Oils that do not mix with water appreciably offer a different, simpler

[1] *Ann. chim. phys.*, [7] 9, 540 (1896).
[2] *Monats. für Chem.*, 30, 759 (1909).

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problem in their drying. In emulsions of these, water must be present as an independent liquid, and have nearly its own vapor pressure. Obviously, no salt can form a stable hydrate having a vapor pressure greater than that of its saturated solution, and this is less than the vapor pressure of pure water. Therefore, a salt shaken in such an emulsion will continue to take up water until it is entirely converted into the highest hydrate it can form at the temperature of the experiment, or until all the water is removed from the oil. The choice of the salt to be used would depend simply on its cheapness and the percentage of water when hydrated. Sodium sulfate answers both these requirements, and seems well adapted to drying this class of liquids.

SHEFFIELD CHEMICAL LABORATORY OF YALE UNIV.,
NEW HAVEN, CONN., May, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

A NEW METHOD FOR THE SEPARATION OF CERIUM.

BY C. JAMES AND L. A. PRATT.

Received June 3, 1911.

Cerium differs from the other elements of the rare earths, in that it forms a series of more highly oxidized compounds. It is a well known fact that many of these ceric compounds very readily undergo hydrolysis, and this property has been made use of for the separation of the element. Cerium material obtained by those methods, which give a precipitate of hydrated ceric oxide, is usually less pure than that obtained from operations giving basic salts. Hitherto, the great disadvantage of precipitating cerium as basic ceric nitrate has been that only a portion of the cerium could be thrown out of solution. The authors have found that potassium bromate is capable of oxidizing cerous nitrate in a faintly acid or neutral solution, so that this element may be entirely separated from the other rare earths.

When a solution of the rare earth nitrates is boiled with potassium bromate in the presence of a lump of marble (saccharoid limestone), the cerium is entirely precipitated as the basic ceric nitrate, with varying amounts of basic ceric bromate. The cerium obtained in this manner is free from other rare earths, if the operation has been carefully conducted.

In working on a large scale with concentrated solutions, it is advisable to use a slight excess of bromate, and to stop the action while a little (about 1 per cent.) cerium remains in the liquid. Under these conditions, a cerium product is obtained which, after washing with a 5 per cent. ammonium nitrate solution, gives a pale straw colored oxide. A saturated solution of the nitrate of this material shows no trace of absorption spectrum when tested with a layer 20 cm. thick.

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Experimental Data.

A solution of pure cerium nitrate was prepared and standardized by precipitating with oxalic acid, and igniting to CeO_2. Ten cc. contained 0.4068 gram CeO_2. In a similar manner a solution of didymium nitrate was made, and standardized. Ten cc. contained 0.4109 gram of the oxide.

Many experiments were performed in the endeavor to find an ideal substance with which to keep the liquid neutral. The results obtained are given below.

(*a*) *Lump Marble.*—Ten cc. of each of the standardized solutions, together with 5 grams of potassium bromate, were diluted to 100 cc., a piece of marble added, and the whole boiled. After a few minutes, a yellow precipitate began to form and free bromine was evolved. The precipitate was filtered, washed with a 5 per cent. solution of ammonium nitrate, and dissolved in hydrochloric acid. It was found necessary to dissolve the precipitate in the beaker previously used, owing to the fact that it was impossible to wash all ceric basic nitrate from the sides of the vessel. The hydrochloric acid solution was boiled, cooled and filtered. The clear filtrate was evaporated to remove the excess of acid, then diluted, and the cerium precipitated as the oxalate. Six experiments carried out in this manner, the time of boiling being varied, gave the following results:

No.	Time. Minutes.	Wt. of CeO_2 (Found).	Wt. of CeO_2 (Theoretical).
1	15	0.3896	0.4068
2	20	0.4083	0.4068
3	25	0.4076	0.4068
4	30	0.4102	0.4068
5	35	0.4123	0.4068
6	45	0.4144	0.4068

Ten cc. of the didymium solution free from cerium were boiled with potassium bromate and marble for 30 minutes and in this case no percipitate formed.

(*b*) *Powdered Marble*, lead carbonate, zinc carbonate, zinc oxide, copper carbonate and copper oxide caused the solution to become rapidly alkaline, which hindered the oxidation by the bromate.

(*c*) *Magnesite* proved to be much slower in its action, and owing to the fact that the mineral lacked uniformity in contour, the basic ceric salts entered the crevices and could not be washed out.

(*d*) *Dolomite* would undoubtedly serve the purpose of ordinary marble, if sufficiently pure. The specimens available for our experiments contained iron, and were unsuited for the work.

The important fact, brought out by the above experiments, and others not included, is that lump marble, presenting, as it does, comparatively

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small surface, is the best material with which to keep the solution in a proper state of acidity for the oxidizing action of the potassium bromate. It should be specially noted that powdered marble is not applicable, as the neutralization is carried so far that the product is contaminated with didymium.

Quantitative Estimation.—Since no satisfactory gravimetric method for the estimation of cerium is known, the authors considered it worth while to attempt to apply this process for quantitative work. In this endeavor, a double precipitation was carried out, using a smooth lump of marble (containing no crevices) so that any adhering precipitate could be easily washed therefrom. The first precipitation was continued until the mother liquor failed to give a test for cerium. This point was determined by withdrawing a small quantity of the supernatant liquid with a pipette, and applying the hydrogen peroxide test. When the liquid was found to be free from cerium, the precipitate was filtered, and washed with a 5 per cent. solution of ammonium nitrate. The filter paper with the precipitate was returned to the beaker, and treated with nitric acid, and a little potassium bromate to oxidize the paper. (It was found absolutely necessary to oxidize all the filter paper, otherwise the cerium could not be precipitated, even after several hours' boiling.) After having boiled the solution to remove the excess of acid, the residue was dissolved in water, and treated as before with potassium bromate and marble. The boiling was continued until the supernatant liquid failed to give a test for cerium. The precipitate was separated on a filter, washed with ammonium nitrate solution, placed in the original beaker, and dissolved in hydrochloric acid. The liquid was then filtered, evaporated to remove the excess of acid, the residue taken up with water, and the cerium precipitated as the oxalate. This was ignited, and the cerium weighed as CeO_2.

The following results were obtained:

	(1)	(2)
CeO_2 found	0.4100	0.4094
CeO_2 present	0.4068	0.4068

The Purification of Cerium on a Large Scale.—The material used for this work consisted of the monazite earths freed from thorium. The oxides were dissolved in nitric acid, the concentrated solution made nearly neutral, heated to boiling, and potassium bromate added. As soon as red fumes of bromine made their appearance, two or three large pieces of marble were placed in the container and the boiling continued for a few hours. The length of the operation depended upon the amount of cerium in the solution. Small portions were withdrawn at intervals, and as soon as it was ascertained by the hydrogen peroxide test that nearly all the cerium had been thrown out of solution, the boiling was discontinued.

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The marble was then removed and the precipitate allowed to settle. The clear supernatant liuqid was syphoned off and the precipitate washed upon a Buchner funnel with a 5 per cent. solution of ammonium nitrate. The basic salt was dissolved in hydrochloric acid and the filtered solution treated with oxalic acid. Sometimes, however, it was found more advantageous to precipitate the cerium as the sulfate by gradually adding concentrated sulfuric acid to the chloride solution, and partially evaporating on the water bath. Alcohol was added to the residue, the sulfate separated by filtration, and washed with alcohol. For a final purification, the sulfate was rendered anhydrous, made into a saturated solution in cold water and once again precipitated by heating.

The small amount of cerium remaining with the other earths in the original mother liquor was next precipitated by boiling with potassium bromate and marble until some of the clear liquid no longer gave the hydrogen peroxide test. This precipitate of cerium carrying a little of the other rare earths was dissolved in nitric acid and added to the next batch for preparation of pure cerium.

The precipitate thrown down by this process varies very considerably, depending upon the conditions of the experiment. It was found, when concentrated solutions were used, that very dense precipitates were obtained. This is a very important point, since the light precipitates, obtained from dilute solutions, filtered with great difficulty. It was impossible to wash even the densest precipitates with water, owing to the formation of colloidal solutions. This difficulty was overcome by washing with a 5 per cent. ammonium nitrate solution. When a large excess of bromate was employed, the cerium was obtained chiefly as a basic ceric bromate. Under the best conditions, using only a slight excess of bromate, a basic ceric nitrate was obtained. On dissolving this precipitate in acid only a slight amount of bromine was evolved.

With too small an amount of bromate, the solution became alkaline, the precipitate darkened in color, and was found to contain didymium, etc. Such a precipitate was purified by dissolving in concentrated nitric acid with the help of a *very little* alcohol. The resulting solution, possessing a deep orange-red color, gave a heavy precipitate upon diluting, and boiling with marble. Care must be taken not to allow the solution to become alkaline by boiling too long.

By the bromate method, the authors obtained many kilograms of cerium salts of such a purity that a saturated solution of the nitrate gave no absorption bands, when observed through a layer 20 cm. thick.

With a little experience, the method is easily controlled and the production of large amounts of pure cerium compounds is only a matter of hours. It would seem that this method might well become commercially valuable as potassium bromate can now be obtained quite cheaply.

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Once again the authors desire to express their thanks to the Welsbach Company for material, through the courtesy of Dr. H. S. Miner.

DURHAM, N. H.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

NEW RARE EARTH COMPOUNDS.

BY L. A. PRATT AND C. JAMES.

Received June 3, 1911.

The salts given in this paper were prepared while searching for some crystallin compounds which might be useful for fractional crystallization of the yttria earths.

Yttrium Methylsulfonate, $Y(CH_3SO_2O)_3.4H_2O$.—In the preparation of this salt, yttrium oxide was dissolved in methylsulfonic acid and the solution evaporated. The residue was taken up in alcohol and precipitated by ether. The compound separated as a viscous mass, which rapidly became crystallin. It was separated from the liquid as far as possible with suction and air-dried. The salt was too soluble to be of value for fractional crystallization.

Calculated: Y, 19.93; S, 21.54. Found: Y, 19.72; S, 21.42.

Yttrium Methenedisulfonate, $Y_2(CH_2(SO_2O)_2)_3.(2^1/_2H_2O?)$.—This compound was prepared by dissolving yttrium oxide in methenedisulfonic acid. The solution was evaporated and treated with absolute alcohol and ether. The resulting precipitate was filtered, washed with ether, and air-dried. The salt is very soluble.

Calculated: Y, 23.87. Found: Y, 23.76.

Yttrium Methinetrisulfonate, $YCH(SO_2O)_3.3^1/_2H_2O$.—This salt was made by dissolving yttrium oxide in methinetrisulfonic acid and evaporating the solution. Upon the addition of alcohol to this liquid, the compound was completely precipitated. It was washed with alcohol with the aid of suction, and air-dried. The salt is insoluble in alcohol and in acetic acid and only slightly soluble in nitric acid.

Calculated: Y, 21.96; S, 23.73. Found: Y, 21.91; S, 24.04.

The methinetrisulfonic acid for this compound was prepared[1] by treating powdered acetanilide with fuming sulfuric acid.

Yttrium Ethylsulfonate, $Y(C_2H_5SO_2O)_3.4H_2O$.—Yttrium oxide was dissolved in ethylsulfonic acid and the solution evaporated. The residue was taken up in alcohol and upon treatment with ether the compound came down in a crystallin form. This was washed on a filter with ether and dried in the air. Like most of the other sulfonates, this compound was very soluble.

Calculated: Y, 18.23. Found: Y, 18.05.

[1] *J. Chem. Soc.*, 75, 280.

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Yttrium Camphorsulfonate, $Y(C_{10}H_{15}OSO_2O)_3 \cdot 7H_2O$.—In order to prepare this salt, yttrium oxide was treated with camphorsulfonic acid and the resulting solution evaporated. The residue was taken up with alcohol and precipitated by ether. The compound came down in a crystallin form, and was filtered off, and air-dried. This substance was found to be very soluble.

Calculated: Y, 9.80. Found: Y, 9.82.

Yttrium Methoxysulfonate.—In an attempt to make yttrium methoxysulfonate, yttrium oxide was dissolved in methoxysulfonic acid and the solution evaporated on the water bath. The residue was dissolved in alcohol treated with an excess of ether. A sticky mass was thrown out, which failed to crystallize under any conditions.

Yttrium Salicylate, $Y(C_6H_4(OH)COO)_3 \cdot 3^1/_2H_2O$.—Since this salt is insoluble in water, it was advantageous in preparing it, to first make the yttrium oxide into the formate and to add to this the required amount of salicylic acid. This mass was boiled until all formic acid was volatilized. The precipitate was then filtered, washed with hot water and dried in the air. The compound was crystallin and very insoluble.

Calculated: Y, 15.81. Found: Y, 15.73.

Yttrium Phthalate, $Y_2(C_6H_4(COO)_2)_3 \cdot 3H_2O$.—To prepare this compound, a known amount of yttrium oxide was dissolved in formic acid and the required amount of phthalic acid added. The resulting mass was boiled to expel all formic acid. The liquid was then decanted off, and the residue boiled for some time with water. It was filtered, further washed with water, and dried in the air. The compound was very insoluble.

Calculated: Y, 24.58; C, 39.77; H, 2.50. Found: Y, 24.55; C, 39.48; H, 2.46.

Yttrium Glycolate, $Y(CH_2OHCOO)_3 \cdot 2H_2O$.—This compound was prepared by dissolving yttrium hydroxide in glycolic acid and heating, when the compound separated out. The precipitate was filtered, washed with water, and air-dried. This salt is practically insoluble.

Calculated: Y, 25.42; C, 20.56; H, 3.74. Found: Y, 25.41; C, 20.23; H, 3.78.

Yttrium Phenylacetate, $Y(C_6H_5 \cdot CH_2COO)_3 \cdot H_2O$.—An excess of phenylacetic acid was added to yttrium hydroxide and heated. The precipitate formed was filtered while the solution was hot, washed with water, and air-dried. This salt was insoluble.

Calculated: Y, 17.38; C, 56.22; H, 4.53. Found: Y, 17.42; C, 56.03; H, 4.42.

Yttrium Phenoxyacetate, $Y(C_6H_5OCH_2COO)_3 \cdot 3^1/_2H_2O$.—For the preparation of this compound, a solution of yttrium chloride was treated with the sodium salt of phenoxyacetic acid and the precipitate washed thoroughly with cold water to separate sodium chloride. The product was further purified by recrystallization from hot water. This compound was only slightly soluble in cold water.

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Calculated: Y, 14.71; C, 47.58; H, 4.66. Found: Y, 14.66; C, 47.80; H, 4.50.

The *phenoxyacetates of Sm, Nd, Pr, La* and *Ce* were prepared in exactly the same manner as the yttrium salt. They were, however, much more insoluble than the latter and therefore could not be recrystallized from water.

$Sm(C_6H_5OCH_2COO)_3.3^1/_2H_2O$.

Calculated: Sm, 22.57; C, 43.20; H, 4.23. Found: Sm, 22.61; C, 43.30; H, 4.03.

$Nd(C_6H_5OCH_2COO)_3.2^1/_2H_2O$.

Calculated: Nd, 22.47. Found: Nd, 22.51.

$Pr(C_6H_5OCH_2COO)_3.1^1/_2H_2O$.

Calculated: C, 46.38; H, 3.90. Found: C, 46.14; H, 4.03.

$La(C_6H_5OCH_2COO)_3.2^1/_2H_2O$.

Calculated: La, 21.82. Found: La, 21.83.

$Ce(C_6H_5OCH_2COO)_3$.

Calculated: Ce, 23.63. Found: Ce, 23.88.

Thorium Phenoxyacetate.—By working with a neutral solution of thorium, the authors found, on the addition of an excess of phenoxyacetic acid, that the thorium was almost quantitatively precipitated. On the other hand, the rare earths behave very differently and are not thrown out of solution, even though a great excess of the acid be added.

This reaction of phenoxyacetic acid on a *neutral thorium* solution affords a method for the separation of this element from the rare earths.

DURHAM, N. H.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

THULIUM I.[1]

BY C. JAMES

Received June 11, 1911.

Thulium was discovered by Cleve[2] in 1879 while trying to separate the element that gives a rose color to the salts of "old erbium." The earths used for this investigation consisted of some material obtained by Nilson while working upon ytterbia. These residues were separated during the use of "the fusion of the nitrate method" and consisted of those portions which were less basic than yttrium but more basic than ytterbium.

Cleve submitted this crude erbia to another long series of fractionations by again fusing the nitrates. This work yielded more basic, intermediate and least basic portions. Thalen examined these fractions spectroscopically for Cleve and showed that old erbia consisted of at least three elements. To the more basic part, which accompanied yttria, Cleve gave the name holmium, and to the least basic, the name thulium, derived

[1] Abstract given before the New York Section, March 10th.

[2] *Compt. rend.*, Sept. 1, 1879.

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from Thule, the old name of Scandinavia. In this paper the oxide of thulium was said to be of a light rose color.

Soret[1] stated that he had observed differences in the absorption spectrum of various fractions of erbium supplied to him by Marignac, and, in the case of holmium, he had provisionally named this element X, as it appeared almost impossible to separate it. In addition it was well known that certain conditions somewhat modified the spectra.

Lecoq de Boisbaudran[1] was of about the same opinion as Soret. He maintained, however, that the thulium red band was rather broader than the ordinary red band of erbium.

Cleve[2] separated 1 ore of the oxide and found it to be white, while its solutions in acids gave colorless salts, which showed two absorption bands, one in the red and one in the blue, the blue band being broad only when the solutions were very concentrated. This material gave an atomic weight of 170.7.

Thalen[3] examined Cleve's purest thulium, which in solution in the form of the nitrate was nearly colorless. It gave a weak erbium absorption spectrum, brilliant lines belonging to ytterbium and about 15 new lines due to thulium. He said: "It seems that a new metal exists, though it must be admitted that it has not yet been separated from ytterbium and erbium."

Lecoq de Boisbaudran[4] recorded the presence of thulium in some fractions.

Krüss and Nilson, in 1887,[5] concentrated thulium, during some of their investigations upon rare earth minerals, so that the absorption bands were stronger than those of erbium. Finding in some solutions that the absorption bands did not show the same relative intensities, they came to the conclusion that thulium consisted of at least two elements: Thulium α, the one giving the band h 684.0, and thulium β, for the one giving the band h 465.0. It is doubtful whether these chemists realized that concentration, acidity, etc., might modify the spectrum, as had been pointed out by some earlier workers.

Crookes,[6] in a paper on the rare earths, described a lot of spectroscopical researches in which a figure for the absorption spectrum of thulium was shown.

Krüss, in 1893,[7] obtained some fractions rich in thulium.

[1] *Compt. rend.*, Sept. 15, 1879.
[2] *Ibid.*, Aug. 9, 1880.
[3] *Ibid.*, Aug. 16, 1880.
[4] *Ibid.*, Sept. 7, 1885.
[5] *Ber.*, 20, 2134.
[6] *Chem. News*, 60, 39.
[7] *Ibid.*, 68, 148.

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Astrid Cleve,[1] during the preparation of some ytterbium material, supposed that a violet color of certain fractions of fused nitrates was due to thulium; she also stated that this element was eliminated only with difficulty from ytterbium.

R. Marc,[2] in a communication on terbium, was of the opinion that thulium was a mixture of ytterbium and yttrium containing varying quantities of holmium and terbium.

C. Auer v. Welsbach,[3] describing a new method for the separation of the ytterbium earths, mentioned the fact that thulium concentrated between erbium and ytterbium, the thulium bands being of greatest intensity in the solutions colored only faintly pink.

About this time the author,[4] working with solutions of the rare earth oxalates in ammonium carbonate, observed that thulium concentrated in the more soluble fractions along with "ytterbium" and some erbium.

Bettendorff[5] considered that the rose color of erbium salts was due to thulium, since he found that the brighter the rose color, the stronger the bands of thulium.

Urbain,[6] in describing the separation of the element lutecium, stated that in fractionating old ytterbium, thulium separated in the least soluble portions.

The writer,[7] giving a new method for fractionating the rare earths, noticed that thulium could be rapidly concentrated in the bromate fractions between erbium and "ytterbium."

Hoffmann and Bürger,[8] when purifying Nilson and Krüss's erbium, found that dilute ammonium hydroxide removed thulium in addition to the ytterbiums.

Urbain[6] mentions the fact that the atomic weight of thulium is not above 168.5.

Extraction.

Since thulium is very rare, it is absolutely necessary to commence with very large amounts of material. In this work the following minerals have been employed: Brazilian monazite (yttrium earths, derived from Brazilian monazite); xenotime; ytterspar (Norwegian xenotime, impure); euxenite; fergusonite (Norway, etc.); yttrotitanite; sipylite (columbate from Northern Norway); gadolinite (Norway and Sweden); also large amounts of oxalates from more soluble double potassium sulfates from

[1] *Z. anorg. Chem.*, 32; *Chem. News*, 86, 248.
[2] *Z. anorg. Chem.*, 27, 304.
[3] *Monatsh.*, [8] 27, 935.
[4] THIS JOURNAL, 29, 495.
[5] *Ann.*, 352, 88; *Chem. News*, 96, 249.
[6] *Compt. rend.*, 145, 759 (1907).
[7] THIS JOURNAL, 30, 182; *Chem. News*, 97, 61.
[8] *Ber.*, 41, 308.

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Carolina monazite, supplied by the Welsbach Co. through the kindness of Dr. H. S. Miner.

The best sources were found to be ytterspar, euxenite, and a columbate from an island in the north of Norway. Gadolinite varied very considerably, some varieties being fairly good, while most were rather poor in the erbium earths. Fergusonite contains only a very little of the desired elements. Yttrotitanite is very troublesome to work up. A specimen of samarskite, presented to the author recently by Prof. F. J. Metzger, Columbia University, was found to resemble euxenite with regard to its content of erbium metals. The details of the processes for the extraction of the mixed rare earths from the various minerals were as follows:

1. *Euxenite.*—The material *was very finely ground* and mixed with an excess of strong sulfuric acid in iron pots of about two gallons capacity. The mixture was then carefully heated until it frothed considerably, after which it was removed from the furnace and stirred rapidly, at which time a vigorous reaction took place. As soon as the evolution of gas began to slacken, the vessel was replaced in the furnace in such a manner that only hot gases from the fire could play upon it, in order that the sulfuric acid might not evaporate too rapidly. When the mass became hard, the iron pot was moved to a much hotter position and kept there until the excess of acid had been driven off. The furnace used was capable of taking four of these iron vessels at one time.

When the operation was successful, the residue had risen, very much like a cake during the baking process, and when in this condition was very readily removed by means of a hammer and chisel. If the operation was not successful, which was usually the case when the pot was left out too long, the whole settled down to a very hard mass which was only removed with great difficulty, so much so that the cast iron vessels were often broken. With very little practice the correct conditions were readily established. The decomposed mineral was powdered, placed in a churn containing water, the churn closed and the contents well agitated.

When the solution was completed, the churn was emptied into a tub and the latter allowed to stand for about twelve hours. After this period had elapsed, the metallic acids were found to have settled so that the clear supernatant liquid could be syphoned off and the rare earths precipitated by means of oxalic acid. The thick mass of columbic acid, etc., remaining at the bottom of the barrel was thrown upon a linen filter and washed with water. Washing by decantation was also very effective.

Sometimes, when the mineral had not been finely pulverized, the decomposition was not complete. In this case the residue was stirred with water and allowed to stand for a short time, after which the liquid, still containing the mineral acids in suspension, was run off from the

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dense, undecomposed euxenite. The latter owing to its density rapidly settles. This coarser material was dried, reground and again worked up. The columbic and tantalic acids were allowed to deposit and the wash water was employed for the solution of more sulfated mineral.

Earthenware vessels were used for the precipitation. (These can be obtained in various sizes. Those possessing round bottoms can be heated by means of steam or calcium chloride baths.)

Fergusonite and Samarskite.—As fergusonite appeared to contain only small amounts of the erbium earths, and, since samarskite resembled euxenite, the writer did not operate upon more than several kilograms. The methods used to attack these substances were: (*a*) By boiling with sulfuric acid containing some potassium sulfate so as to increase the temperature. (*b*) Hydrofluoric acid.

When using sulfuric acid and potassium sulfate it was found necessary to stir well during the hardening, as otherwise the whole solidified to a cement-like mass. The result of the reaction after powdering was treated with ice-cold water, filtered and the clear filtrate precipitated with oxalic acid.

The hydrofluoric acid method was found to be an excellent one, inasmuch as the mineral need not be so finely ground. However, the cost was a great drawback, to obviate which the author prepared the acid on a large scale by using a capacious iron retort fitted with a leaden cover. The condenser consisted of a large lead pipe running through a barrel of water. The top of the condenser was so formed that water could drip in a sufficient quantity to form a concentrated, fuming acid.

Columbates.—Some columbates are attacked only with great difficulty by sulfuric and hydrofluoric acids while they are very rapidly decomposed by means of sodium hydroxide in the fused condition.

The mineral used resembled sipylite. It was much richer, however, in rare earths, since it contained about 43 per cent.

ANALYSIS.

Cb_2O_5 (trace Ta_2O_5)	42.42
SiO_2	4.27
WO_3,SnO_2	0.37
ZrO_2	0.41
Cu group	1.38
U_3O_8	1.40
Fe_2O_3,Al_2O_3	1.55
Yttrium earths	39.91
Cerium earths	3.57
ThO_2	1.10
CaO	1.25
MgO	0.07
Loss upon ignition (H_2O, He, etc.)	2.00
	99.70

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This mineral, which was of a reddish brown color, came from an island in the north of Norway. It possessed endothermic properties, since upon heating it soon began to glow. This glow rapidly passed through the mass. After cooling, it was observed that the mineral had become yellowish, more opaque, and could easily be powdered. Its sp. gr. before heating was 5.30 and after heating 4.62. The atomic weight of the yttrium earths was found to be about 110.2.

The analysis and other determinations were carried out very carefully by Mr. H. P. Corliss, to whom the author wishes to express his thanks.

In order to separate the earths, the mineral was first ignited, powdered, mixed with twice its weight of sodium hydroxide and carefully fused for about two hours. The liquid mass was then poured upon an iron plate. The cold melt was next broken in pieces and allowed to stand in contact with water, until it assumed the appearance of mud. It was then mixed with hot hydrochloric acid and the whole heated upon the water bath.

The columbic acid, etc., was then filtered off and the rare earths precipitated by means of oxalic acid.

Yttrotitanite.—Hydrochloric acid was used for attacking this substance. The mineral was finely powdered and heated with the acid for a considerable period. The acid liquid was filtered and the small amount of rare earths present precipitated as the oxalates. A large excess of acid was always avoided.

Ytterspar.—(Impure Norwegian xenotime.) The best method for decomposing this mineral was found to be as follows:

Sodium hydroxide was mixed with a little less than half its weight of water in an iron pot, the temperature raised to the boiling point and powdered ytterspar, equal in weight to the sodium hydroxide employed, was added. It was then stirred until the charge solidified, after which the temperature was raised to a low red heat. The result of the reaction was very friable and readily removed from the containing vessel. The crumbled material was mixed with water, boiled and filtered. The hydroxides, titanic acid, gangue, etc., remaining upon the filter were well washed with boiling water. The green filtrate usually became thick, owing to the mass of crystals (phosphates) which separated as the liquid cooled. The hydroxides were treated with a slight excess of hydrochloric acid, the solution was filtered and the earths were separated by the use oxalic acid.

Gadolinite was decomposed by heating with hydrochloric acid. The earths were obtained in the usual well-known way.

As the ytterspar earths contained only a very little of the elements of the cerium group, they were converted directly into the bromates in the following manner:

The crude oxides, obtained by igniting the oxalates, were dissolved

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in hydrochloric acid, the solution diluted, filtered, and precipitated by oxalic acid. The oxalates were converted into sulfates by the action of concentrated sulfuric acid. The anhydrous sulfates were dissolved in cold water. The solution was then poured upon barium bromate covered with a layer of water and heated upon the water bath.[1] When the decomposition was complete, the barium sulfate was filtered off and the bromates fractionally crystallized.

The earths from euxenite, gadolinite, etc., which contained members of the cerium group, were first subjected to the sodium sulfate treatment.[2] After separating the insoluble double sulfates, the solution was precipitated by means of oxalic acid and the yttrium earth oxides, obtained by igniting the oxalates, were converted into bromates in a similar manner to the crude ytterspar oxides described above.

After the bromates had been fractionated for some time[3] it was found that nearly all the erbium had accumulated in the more soluble fractions, nearly all of which were quite free from the absorption bands of holmium and dysprosium. Since terbium was less soluble than dysprosium, and since the oxide had the pure rose tint of erbium, it was evident that the material was quite free from the terbium. The separation of ytterbium and lutecium from erbium was found to be very rapid. Five crystallizations of a mixture of erbium, thulium, ytterbium and lutecium, which possessed a fine rose color together with a strong erbium absorption spectrum, left most of the material in the mother liquor as a colorless liquid. The absorption bands of erbium and thulium were very faint, when observed through a saturated solution 5 cm. thick.

Thulium separated fairly rapidly and collected in the fractions between erbium and ytterbium as the crystallization was continued. Whenever the thulium bands became intense, the fraction was placed aside until no more would separate from the series. The less soluble fractions consisted of erbium with some yttrium.

The more soluble portion was then taken and again submitted to fractional crystallization. This portion was nearly colorless. It showed the absorption bands of thulium together with a very weak spectrum of erbium. It was apparent that by far the greater portion consisted of ytterbium and lutecium with perhaps traces of scandium. Of this crude material there was nearly three kilograms. The work was carried out in a room that possessed a fairly constant temperature of about 60° F.

[1] THIS JOURNAL, 30, 182.

[2] In using sulfate of sodium in place of sulfate of potassium care must be taken not to employ a great excess, otherwise some of the yttrium earths will be precipitated also. Yttrium sodium sulfate is rapidly decreased with regard to its solubility after the concentration of the sodium sulfate has reached a certain point. This problem has been partly studied, and the solubility curve, etc., will be published shortly.

[3] THIS JOURNAL, 30, 990.

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Higher temperatures were not suited for the work, since they tended to prevent crystallization, of the more readily soluble fractions.[1] Casseroles were the vessels employed and the concentration was so gauged that the major portion separated in the crystallin form.

Since the more soluble bromates crystallize rather sluggishly, they were first crystallized once a day. However, when the most soluble portion had been removed, two operations could be carried out daily.

Because the salts form supersaturated solutions with extreme ease, it was absolutely necessary to start the crystallization with a crystal.

During the first few series of operations, erbium rapidly separated leaving the more soluble portions colored greenish. As the work proceeded, thulium concentrated in the fractions next to the least soluble erbium. When the mother liquors were found to be free from thulium they were placed aside. The color shown by these bromates in solution was of a yellowish green, which was afterwards found to be due to copper. Scandium occurred in these fractions in the merest traces only. This latter element was more inclined to separate with the erbium. This was, perhaps, due to the fact that the solutions became slightly basic. After all copper and other impurities had been removed, the fractions, more soluble than thulium, became colorless and formed good crystals.

The most interesting portion of the series was where the thulium accumulated. When free from erbium the solutions possessed a bluish green color. After sixteen weeks of this stage of the fractionation the colors of the various fractions, from the least soluble to the most soluble, were rose, yellow, bluish green, colorless and finally those colored yellowish green (copper). The yellow tint was due to admixture of erbium and thulium.

When the fractions became too small to recrystallize from water, a mixture of alcohol and water was used with good results.

After continuing the work it was observed that the thulium fractions did not change in color, simply remaining of a greenish tint when in solution. The presence of a very little erbium has a marked influence upon this color, since a trace turns it yellowish green, a little more renders it colorless and further addition pink. As the fractionation progressed it was evident that the alcohol was being slowly attacked by the bromates. This decomposition increased; the liquids became colored and smelled strongly of bromine and ethyl acetate. At this point the fractions were united according to color and precipitated as the oxalate. The oxalate was of a very pale green tint when moist. Artificial light increased this tint so that it became a delicate pale green color. The oxide, ob-

[1] The bromates should be free from impurities, since metals, which form bromates not isomorphous with the rare earths, cause the formation of tiny crystals so that it is practically impossible to drain off the mother liquor.

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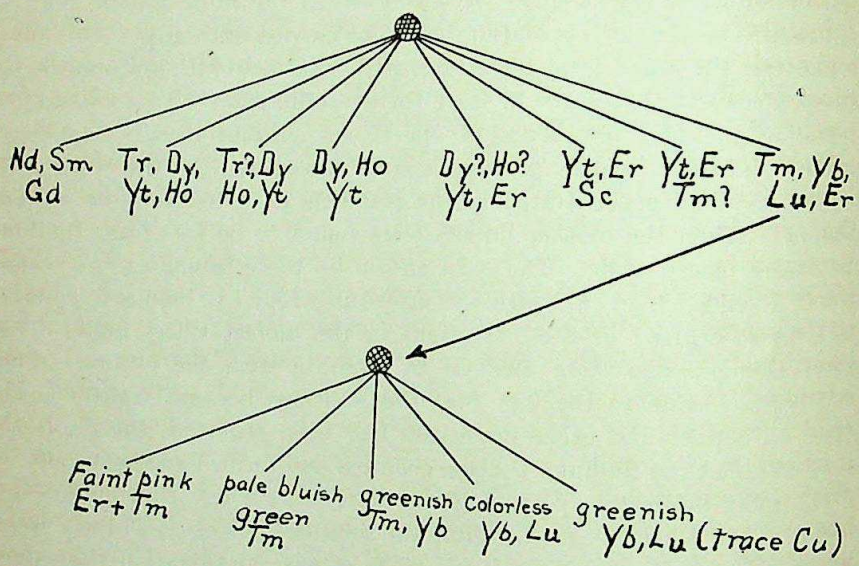
tained by igniting this oxalate, also showed this green tint and yielded a carmine glow, when heated carefully by a Bunsen burner.

The extraction of thulium commencing with the crude ytterium earth bromates will be better understood by the following diagram:

CRUDE YTTRIUM EARTH BROMATES.



Some thulium oxide, containing ytterbium, was dissolved by heating with concentrated nitric acid for a short time, a large excess of concentrated nitric acid added and the boiling liquid fractionally precipitated by means of a boiling saturated solution of oxalic acid. Oxalic acid was added until a permanent precipitate formed, when the liquid was well stirred and cooled. The crystallin oxalate was removed by filtration and the filtrate again heated and treated with more oxalic acid solution and so on. The final mother liquor was evaporated nearly to dryness, taken up with water and all earths thrown out as oxalates.

After a number of series of precipitations had been carried out, some of the oxides from the first and last fractions were dissolved in concentrated hydrochloric acid and the spark spectrum photographed. The negatives obtained showed that there had been practically no fractionation, as the lines were identical in relative intensities.

The picrates were next tried. Thulium oxide similar to that used for the previous experiment was converted first into the hydroxide and then into the picrate. The solution of the picrate was then evaporated and fractionally crystallized. After six series, the first and last fractions were compared by the use of a spectrograph. The photograph showed scarcely any change in the lines.

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One of the least soluble thulium bromate fractions, which contained a little erbium, was converted into the oxalate. This oxalate was fractionated by the oxalate-carbonate method. The results showed that this procedure was not rapid enough to be of any value.

In addition to these methods several others were tried, but none could be compared with the bromate method.

Since yttrium bromate comes between the bromates of praseodymium and neodymium, with regard to their solubility in water, and because the bromate of praseodymium is more soluble than the corresponding compound of yttrium,[1] it was considered that by crystallizing a mixture of erbium, thulium and praseodymium bromates, praseodymium would come between erbium and thulium. An experiment along this line showed that praseodymium rapidly accumulated in the least soluble fraction. However, by gradually feeding this substance through the most soluble fractions, they were kept larger and the erbium was swept out. Owing to the rapidity, with which praseodymium separated from erbium, it was thought advizable to try a mixture of the bromates of yttrium and praseodymium carrying small amounts of erbium and neodymium. The results were surprizing, as the praseodymiu again appeared in the fractions less soluble than yttrium. According to the solubilities, as previously mentioned, yttrium should be more soluble than neodymium but less soluble than praseodymium. The solubilities had been determined at 25°, while the crystallizations had been carried out at room temperature. The solubilities of lanthanum bromate and praseodymium bromate in yttrium bromate solution will be studied at the earliest opportunity.

A specimen of the purest thulium so far obtained by the bromate method was sent to Sir William Crookes who examined it by means of the spectrograph. He said: "Spectroscopic analysis shows very good thulium, and a trace of ytterbium. Only a very faint trace of calcium is present." The writer is extremely grateful to Sir William Crookes for his kindness in testing this and many other specimens.

These purest fractions were again converted into the bromate and fractionated first from water solution and then from aqueous alcohol. Later, a mixture of methyl and ethyl alcohols was tried. By employing methyl alcohol in place of water it was hoped that the decomposition of the bromates would be prevented. After working for a short time the liquid became colored, and a crystallin compound, insoluble in the mixed alcohols, was deposited. This compound was soluble in water, and evolved bromine when acidified with hydrochloric acid.

The various fractions were mixed according to their purity, the purest product being reserved for a determination of the equivalent,

[1] THIS JOURNAL, 31, 913.

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which will form the main subject of the next paper on thulium. The fractions not quite so pure were used for the preparation of many compounds, some of which are given below.

The most important point proved by this work is that the element, giving the characteristic absorption bands of thulium, cannot be separated into simpler substances. After about 15,000 operations the absorption spectrum underwent no change.

Compounds of Thulium.

Thulium Oxide, Tm_2O_3, was prepared by igniting the oxalate. It forms a dense white powder with a faint green tint. This oxide dissolves slowly, if heated with strong acids, and, when carefully made to incandesce, emits a carmine colored glow.

Thulium hydroxide as usually obtained forms a precipitate which settles very readily, and filters nicely even when thrown down in the cold. This compound dissolves easily in dilute acids.

Thulium Bromate, $Tm_2(BrO_3)_6.18H_2O$, was obtained by decomposing barium bromate, covered with water, and heated upon the water bath, with a solution of thulium sulfate. As soon as the supernatant liquid failed to give a test for sulfuric acid, the barium sulfate was filtered off, and the filtrate concentrated. As the liquid cooled, the salt separated in pale, bluish green prisms belonging to the hexagonal system, and isomorphous with the other rare earths.

The bromate was obtained in nice small crystals by pouring a saturated solution into an excess of 95 per cent. alcohol. After standing a short time the liquid became full of crystals, which upon analysis gave the following results:

	Tm_2O_3.	Br_2O_5.	H_2O (diff.).
Calculated (Tm = 168.5)	26.95	50.37	22.68
Found	27.08	50.34	22.58

Ammonium hydroxide was found to be the best precipitant. The thulium hydroxide must be well ignited, as otherwise the results run a little high. The oxalate gave figures that were slightly low, indicating a tendency of the oxalate to dissolve in dilute acid.

Thulium Chloride, $Tm_2Cl_6.14H_2O$.—Thulium oxide was dissolved in concentrated hydrochloric acid, and the solution evaporated until crystals formed upon the surface. It was then placed in a desiccator over sulfuric acid, until a quantity of the chloride had crystallized out. The crystals were pressed between thick filter paper under a press. The nearly dry chloride was finally freed from moisture over sulfuric acid. This compound which possessed a green tint was very soluble in water and alcohol. When 0.4 gram was dissolved in 100 cc., a distinct absorption band in the red could be seen using a layer 5 cm. thick.

Analysis—Calculated: Tm_2O_3, 48.06. Found, 48.26.

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Thulium Sulfate, $Tm_2(SO_4)_3.8H_2O$.—In order to obtain this salt, some oxide was dissolved in a slight excess of hydrochloric acid. The solution was diluted somewhat, an excess of sulfuric acid added, and the whole poured into an excess of 95 per cent. alcohol. The resulting product was very milky and after a few minutes crystals began to form. When it had stood for some time the sulfate settled. It was filtered off and washed with alcohol to remove all traces of hydrochloric and sulfuric acids. The anhydrous sulfate was easily obtained by carefully heating the hydrated compound nearly to redness. When the anhydrous compound was added to water, it formed a sticky mass at the bottom of the beaker, which, however, rapidly dissolved. The neutral sulfate solution seemed to be more astringent, but less sweet, than a corresponding solution of ytterbium.

The hydrated sulfate gave 18.80 per cent. H_2O, and the anhydrous salt 61.52 per cent. Tm_2O_3, upon analysis. These results show that the amount of water of crystallization is similar to that of most of the other rare earth sulfates, *viz.*, 8 H_2O.

Thulium Oxalate, $Tm_2(C_2O_4)_3.6H_2O$, is obtained as a white precipitate with a greenish tint by treating a slightly acid solution of thulium with a solution of oxalic acid. Using hot solutions an oxalate was prepared possessing the following composition:

	Tm_2O_3.	C_2O_3.	H_2O (diff.).
Calculated	54.30	30.46	15.24
Found	54.20	30.35	15.45

This salt is soluble in potassium and ammonium oxalates, owing to the formation of double salts. These double oxalates have been used by Auer von Welsbach for separating the members of the yttrium group. The author found this procedure to be more troublesome and very much slower than the bromates.

Thulium Acetylacetonate, $(CH_3COCHCOCH_3)_6Tm_2.2H_2O$.—This compound was prepared by precipitating a solution of thulium chloride by an excess of ammonium hydroxide, washing the precipitate first by decantation, then on a Buchner funnel, and finally dissolving the hydroxide in a warm mixture of absolute alcohol and acetylacetone. Thulium hydroxide dissolved with great ease in the above mixture. On evaporating the solution, the salt separated. This was purified by recrystallizing from absolute alcohol. It was not volatil in a vacuum.

The acetylacetonate gave 40.02 per cent. Tm_2O_3 upon ignition, which indicates that there are two molecules of water of crystallization present.

Some thulium material carrying a little ytterbium (neoytterbium) was converted into the acetylacetonate and submitted to several series of fractional crystallizations. The most soluble and least soluble portions showed a slight difference in the spectrograph. Unfortunately this com-

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pound readily undergoes hydrolysis and for this reason it cannot be used for purifying thulium.

The absorption spectrum of an alcoholic solution of the acetylacetonate differs from aqueous solutions of other salts, such as the nitrate and chloride. The difference is shown more especially by the blue band, which in the case of the acetylacetonate is most intense on the side towards the red, whereas the nitrate in aqueous solution gives the most intense part on the violet side.

Thulium Phenoxyacetate, $(CH_2(C_6H_5O)COO)_6Tm_2.6H_2O$.—Thulium hydroxide was dissolved in a solution of phenoxyacetic acid in dilute alcohol. The clear liquid was evaporated, the crystals were separated upon a Hirsch funnel and washed with water. The crystallin mass was well stirred with 95 per cent. alcohol after which an equal volume of ether was added. The phenoxyacetate was again filtered and washed with ether. This compound is very voluminous, sparingly soluble in water and soluble in alcohol. By a simple ignition it was found that the thulium oxide amounted to 28.58 per cent.

Thulium Nitrate, $Tm_2(NO_3)_6.8H_2O$.—This was obtained by dissolving thulium oxide in nitric acid and evaporating to a small bulk. After a slight excess of fuming nitric acid had been added, the nitrate crystallized out. This compound is deliquescent. When it was dried over sulfuric acid and analyzed, it gave the following results: Tm_2O_3 = 45.24 per cent.; calculated Tm_2O_3 = 45.12. This compound therefore contains eight molecules of water of crystallization. Most of the rare earth nitrates contain ten or twelve molecules of water. Thulium nitrate resembles "old ytterbium" nitrate, since Astrid Cleve gave 8 H_2O as the amount of hydration of the latter salt.

Thulium nitrate can readily be crystallized from nitric acid. The fractionation of the simple nitrates from nitric acid was first proposed by Demarcay and since then has been used with great success by Urbain and others. At this end of the series the nitrates are very soluble and strong nitric acid must be used during the fractional crystallization.

DURHAM, N. H.

VOLHARD'S METHOD FOR THE ESTIMATION OF CHLORINE IN POTABLE WATERS.

BY A. T STUART.

Received May 22, 1911.

The Volhard method, as is well known, requires the addition of an excess of standard silver nitrate solution to the sample under investigation. The precipitated silver chloride is filtered off and the excess of silver nitrate remaining in the filtrate is determined by titration with standard potassium thiocyanate, using a ferric salt as indicator.

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It has been suggested that this method be adopted for the determination of chlorine in drinking waters where exceptional accuracy is desired and where the end point by the "Chromate" method is obscured or interfered with by natural color and dissolved peaty matter in the water.[1] In applying this method to water of this type the writer encountered discrepancies which invited further investigation.

Solutions were made as follows:

Silver nitrate of such strength that 1 cc. = 0.001 gram chlorine; *potassium thiocyanate* of equivalent strength; *nitric acid* freed of oxides of nitrogen by boiling.

The *indicator* was prepared by dissolving a known amount of $FeSO_4 . 7H_2O$ in water, oxidizing with nitric acid, evaporating to dryness with sulphuric acid and neutralizing the excess of this with ferric carbonate and filtering. The filtrate was so diluted that the solution contained 1 per cent. $Fe_2(SO_4)_3 . 9H_2O$.

Titrations were made in a flat porcelain dish and the volume always kept constant. A similar dish was placed alongside in which a like amount of silver thiocyanate was precipitated. This aided in the determination of the end point. In all cases 2.00 cc. silver nitrate (representing the excess in any determination) were run in from a 2 cc. pipette graduated to $^1/_{50}$ cc. The indicator was carefully measured in each case and the potassium thiocyanate run in from a similar pipet of 2 cc. capacity. Five cc. of nitric acid were added in each case.

READINGS TABULATED.

Water.	Indicator.	KCNS.	Water.	Indicator.	KCNS.
100	0.1	4.0?	95	5.0	1.92
100	0.2	3.0?	95	6.0	1.90
100	0.3	2.6?	95	7.8	1.90
100	0.4	2.4	93	8.0	1.87
100	0.5	2.3	90	10.0	1.80
100	0.6	2.2	85	15.0	1.75
100	0.7	2.15	80	20.0	1.60
100	0.8	2.15	75	25.0	1.51
100	0.9	2.12	70	30.0	1.44
100	1.0	2.09	65	35.0	1.35
100	1.2	2.07	60	40.0	1.25
100	1.4	2.05	50	50.0	1.05
100	1.6	2.05	40	60.0	0.86
100	1.8	....	30	70.0	0.67
100	2.0	2.05	20	80.0	0.48
100	2.5	2.02	10	90.0	0.28
100	3.0	2.00	..	100.0	0.08
	4.0	1.94	..	104.0	....
			..	110.0	....

[1] "The Volhard Method for the Determination of Chlorine in Potable Waters." Shutt and Charlton, Proceedings Royal Society, Canada, 1905.

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These results are plotted in Fig. 1.

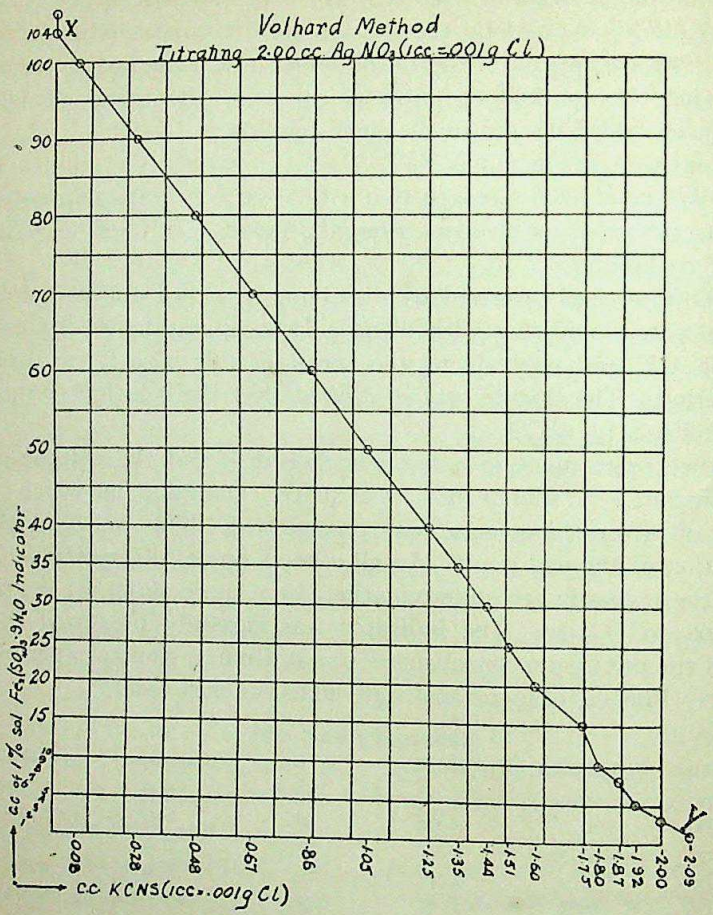

Fig. 1.

The above curve includes all cases of course, both extreme and otherwise, but clearly illustrates the influence of "mass action," whereby it is seen that if the concentration of the ferric salt is so increased it will completely drive the reaction in the other direction and leave the silver nitrate unacted upon. In applying this method it was expected that the silver thiocyanate formed, being insoluble, would be precipitated out of the phase in which the reaction takes place and thus allow it to go in the one direction. However, it is considered that the small amount remaining in solution sets up a series of equilibria which are represented in the curve. Referring to Fig. 1, at the point "Y," close to the axis, the concentration of the ferric salt is very low and hence the reaction is almost complete between:

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$$AgNO_3 + KCNS = AgCNS + KNO_3.$$

At the point "X," near the axis, the concentration of the ferric salt is very great and the first addition of potassium thiocyanate reacts with the ferric salt to give a red color:

$$Fe_2(SO_4)_3 + 6KCNS = 2Fe(CNS)_3 + 3K_2SO_4.$$

At points between "X" and "Y" there is a series of equilibria set up representing a combination of the two equations:

$$\left.\begin{matrix} AgNO_3 + KCNS \\ Fe_2(SO_4)_3 + 6KCNS \end{matrix}\right\} \begin{matrix} \longrightarrow \\ \longleftarrow \end{matrix} \left\{\begin{matrix} AgCNS + KNO_3 \\ 2Fe(CNS)_3 + 3K_2SO_4 \end{matrix}\right.$$

The end point of the reaction is also necessarily influenced to a certain extent by the dissociation in solution of the red ferric thiocyanate, represented as follows:

$$\underset{\text{(undissociated)}}{\overset{\text{red}}{Fe(CNS)_3}} \rightleftharpoons \overset{\text{colorless}}{Fe^+} + \overset{\text{colorless}}{(CNS)^-}.$$

(dissociated ions)

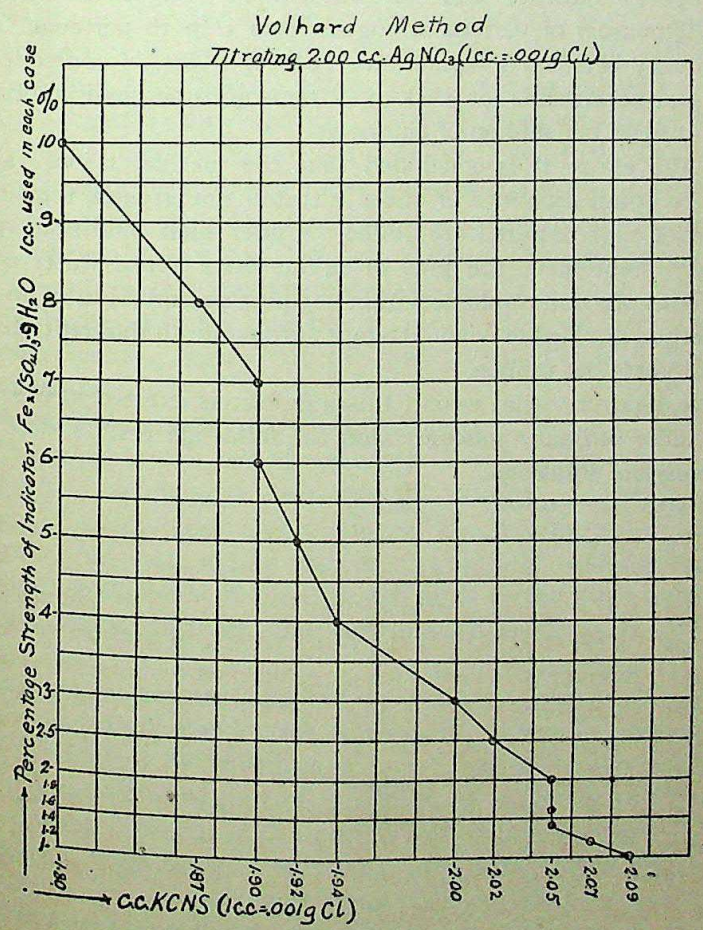

Fig. 2.

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Thus on the addition of the *first slight* excess of potassium thiocyanate a red color may not be produced since the concentration of the ferric thiocyanate is so low that it is completely dissociated into colorless ions and the undissociated, and red ferric thiocyanate may not be formed until the concentration of the $(CNS)^-$ ion drives the reaction in that direction. This point is indicated by the curve in Fig. 1, for at the extremity "Y" it is found necessary to add potassium thiocyanate even to the extent of 3 and 4 cc. On the other hand, at the extremity "X," where the concentration of the Fe ion is very great, the slightest addition of $(CNS)^-$ ion immediately reacts to form the undissociated red ferric thiocyanate.

To eliminate extreme cases and further illustrate results within practical working limits a second curve is drawn. One axis represents *one cc.* of indicator of various per cent. strengths and the other the potassium thiocyanate required.

The figures indicate that in titrating 2 cc. silver nitrate, using 1 cc. of indicators of various strengths from 1 to 10 per cent., the reading may vary between 1.80 cc. and 2.09 cc. This, of course, represents an error not permissible for work of extreme accuracy and involving in its limits 2.9 parts per million of chlorine.

From the above it is concluded that the method is only applicable when very small amounts of silver nitrate—not greater than 0.2 cc.—in excess of that required are added. Under such conditions and those previously mentioned, the plus or minus error for a water containing say 10 parts per mil. would be within 0.5 part per mil., but in no such case is the method applicable when attempts are made to differentiate between fractional parts per million.

To investigate to what extent this influence is exerted in cases of solutions of more ordinary concentration the following results were obtained with *decinormal* solutions:

Water.	HNO_3.	$AgNO_3$.	Indicator.	KCNS.
100	5	2	0.1	2.5?
100	5	2	0.5	2.05
100	5	2	1.0	2.00
100	5	2	5.0	1.95
90	5	2	10.0	1.92
75	5	2	25.0	1.87
50	5	2	50.0	1.70
25	5	2	75.0	1.58
..	5	2	100.0	1.42
90	5	10	1.0	10.05
80	5	10	10.0	10.00
65	5	10	25.0	9.85
50	5	10	50.0	9.70
..	5	10	100.0	9.50
65	5	25	10.0	24.70
..	5	25	100.0	24.30

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Although a variance is quite noticeable when examining solutions of *ordinary* strength, it may not be considered of sufficient practical importance to seriously interfere with the use of this method. It would, however, be necessary to take particular care that a very slight excess only of silver nitrate is present.

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THE SIGNIFICANCE OF THE PERIODIC LAW.

BY FERNANDO SANFORD.

Received June 13, 1911.

The physical significance of the periodic law has been the subject of much speculation and of many important investigations. The conclusion seems inevitable that the chemical elements have been built up step by step, from some simpler substance or substances, but thus far all attempts at identifying the original substance have failed. Meanwhile, the discovery of radioactivity and the successive disintegrations of the uranium and thorium atoms seem to have shown us how these atoms were originally put together. In this process we see one elementary atom changing into another of lower atomic weight by releasing one or more alpha particles or one or more negative electrons, or in some cases, perhaps, by giving off both an alpha particle and an electron in a single change. Since the electron has but little, if any, influence upon the atomic weight, we find these successive atoms differing in atomic weight by four or eight, or in the case where only an electron is set free we may have two successive atoms with the same atomic weight but with different chemical properties.

Since the disintegration products of uranium seem to fall into their proper positions in the periodic series and to have properties analogous to the other members of their periodic groups, radium, for example, showing the characteristic properties of the barium group and emanation forming an inert gas of the argon group, it would seem to follow that the other elements of these groups must in the same way be formed by adding alpha particles and electrons to elements of lower atomic weight.

A difficulty in constructing the elementary series in this way arises from the fact that the atomic weights of successive elements do not increase by four or by multiples of four. This difficulty is largely overcome for a considerable part of the series, by assuming two parallel lines of development, one line starting from helium and one from lithium. In the following table the elements have been arranged in two series from that point of view, the attempt being made to select the elements which would most nearly meet the atomic weight requirements:

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		He	Be	C	O	Li	B	N	F
		4	9	12	16	7	11	14	19
		Ne	Mg	Si	S	Na	Al	P	Cl
		20	24	28	32	23	27	31	35½
		A	Ca	Ti	Cr	K	Sc	V	Mn
		40	40	48	52	39	44	51	55
Fe	Ni	Co	Zn	Ge	Se	Cu	Ga	As	Br
56	59	59	65	72	79	63	70	75	80
		Kr	Sr	Zr	Mo	Rb	Yt	Nb	(Cb)?
		82	88	90½	96	85½	89	94	93½
Ru	Rh	Pd	Cd	Sn	Te	Ag	In	Sb	I
102	103	106	112	119	127	108	114	120	127
		Xe	Ba	Ce	Pr	Cs	La	Nd	Sa
		128	137	140	140½	133	142	144½	150
		...	...	...	...	Eu	Gd	Tb	Dy
		...	...	...	...	152	156	159	162
		...	...	...	W	Er	Yb	Lu	...
					184	167½	172	174	...
Os	Ir	Pt	Hg	Pb	Po	Au	Tl	Bi	...
191	193	195	200	207	(210)?	197	204	208	
		...	...	...	...	...	...	...	...
		Em	Ra	...	U	...	Th		
		222	226		238		232		

Starting with helium, it will be seen that the series is regular up to and including iron, Be being the only element whose atomic weight does not conform to our requirements, its atomic weight being 9 instead of 8. With the occurrence of the triplets Fe, Ni, Co, the orderly arrangement is broken up, though the preponderating influence of the quantity four may still be observed. Thus the increase in atomic weight from cobalt to rhodium is 44 and from rhodium to osmium 88. If the lowest atomic weight in a column be subtracted from the highest above the first series of missing elements, we have Xe — He = 124, Ba — Be = 128, Ce — C = 128, and Pr — O = 124½.

In the disintegration of uranium three alpha particles seem to be given off between uranium and radium, allowing an element of atomic weight 234 or 230 to fall in the carbon group, and one alpha particle is given off between radium and emanation, bringing the latter in its appropriate group of the argon gases. The proper positions of the other disintegration products are unknown to me.

The table also indicates that another radioactive series starts from tungsten with Pr as probably its last element.

In the lithium series the agreement with theory is about equally good throughout with that of the helium series. The irregularity begins at about the same atomic weight and is about equally great, though there seem to be more recurrences of six as a difference between two successive atomic weights. In both series these irregularities begin where each

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group of the series seems to split into two groups, as the group of the alkali metals and the copper, silver and gold group. These irregularities offer a serious difficulty to the acceptance of the theory of atomic development outlined here.

In the lithium series the radioactive group, which is assumed to start from tungsten in the helium series, is represented by a succession of very rare elements whose rarity suggests that they are also unstable, and the radioactive group starting from uranium is represented by a similar group starting from thorium. I have not attempted to represent the position of any of the products of thorium disintegration, as I am not sufficiently familiar with their properties, and it is altogether probable that other elements are placed in wrong groups.

It is well known that certain fundamental differences seem to exist between the two groups of elements which are here characterized as the helium series and the lithium series. The two series have, in fact, long been separated on the basis of their chemical valency, the elements of the helium series having zero valency or even valencies, while the elements of the lithium series have odd valencies. They have likewise been separated on the basis of their spectra, the elements of the helium series having their spectral series made up of single lines or groups of three, while the elements of the lithium series have their spectral lines arranged in pairs. From the researches of Sir Norman Lockyer and others on the spectra of the stars, it would seem that in the hottest stars only elements of the helium series are found, several of these elements apparently appearing before any of the lithium elements appear. Thus calcium and iron are said to appear before sodium.[1]

This hypothesis as to the structure of the elementary atoms suggests a possible cause of radioactivity and the possibility of artificially changing one element into another. The alpha particle is known to be very strongly electropositive, and the elements of at least some of the groups become increasingly electropositive as their atomic weights increase. I have attempted elsewhere to show that many of the elements carry positive charges which are proportional to the square roots of their atomic weights.[2] As their electropositive charges increase their hold upon the alpha particles must decrease, and the heavier elements must accordingly become more and more unstable. This hypothesis seems to gain probability from the fact that in the radioactive disintegration of uranium eight alpha particles and only four electrons seem to be set free in changing a uranium atom to one of lead. If this be the correct explanation of their instability it does not seem impossible that by submitting an atom of an electropositive metal to a powerful electropositive stress it may

[1] Messrs. Jessup, *Phil. Mag.*, 15, 21, Jan., 1908.
[2] On Positive Atomic Charges, *Phys. Rev.*, 32, 512, May, 1911.

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be made to throw off an alpha particle and become an atom of some element of lower atomic weight. Thus the sodium atom by giving off an alpha particle might become a fluorine atom, or a potassium atom might in the same way become a chlorine atom. In fact, there seems to be some evidence that alpha particles have been given off from metals in this way, and that many of the phenomena of the *Kanalstrahlen* can best be explained by the assumption that some of them are alpha particles sent off from the anode.

Thus in an article on "Rays of Positive Electricity,"[1] Sir J. J. Thomson calls attention to the fact that while the particles which constitute the *Kanalstrahlen* have different velocities after passing through the cathode their maximum velocity (presumably for anodes of the same metal) is always the same, regardless of the fall of potential along the tube. This velocity was previously found to be 2×10^8 cm./sec. whether the fall of potential in the tube was 3,000 volts or 40,000 volts. It was also shown that their velocity was much greater than could be given to them by the electric field of the tube. Similar positively charged particles were also sent off from the cathode with the same speed as from the anode, though they had to travel against the electric field of the tube throughout the whole of their path.

The ratio of charge to mass was determined for the particles which constituted the *Kanalstrahlen* by passing them through an electrostatic and a magnetic field after they had passed through the cathode. The particles were sorted into seven quite distinct groups by this method, each group producing its own fluorescent patch on the screen at the end of the tube. These groups are indicated on p. 759 of the article referred to by the letters *a*, *b*, *c*, *d*, *e*, *f*, while the central fluorescent spot which was made by undeflected particles is not indicated by a letter. The values of e/m determined for these groups of particles seem to the present writer to indicate that three of them were due to alpha particles. Thus the value of e/m for the group marked *d* was determined as 5.8×10^3. The ratio e/m for the alpha particle as determined by Rutherford, and Geiger[2] varied from 4.8×10^3 to 5.7×10^3. This would seem to make it almost certain that patch *d* was caused by alpha particles.

The positive charge of an alpha particle is almost exactly twice as great as the negative charge of an electron, so that when two electrons unite with an alpha particle to form a helium atom they give the most completely electrically neutral particle known. This is shown chemically by the fact that the helium atom has less affinity or cohesion than any other known atom. Accordingly, when an alpha particle has taken up one electron its ratio e/m must be exactly half what it was before, and

[1] *Phil. Mag.*, 19, 424.
[2] *Proc. Roy. Soc., London* (*A*), 81, 162.

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an alpha particle which captured an electron before it reached the cathode would have a value $e/m = 2.9 \times 10^3$. This value was actually determined for the particles which produced patch *c*.

There still remains the probability that a considerable number of alpha particles would combine with two electrons and form neutral helium atoms before reaching the cathode, and these would be undeflected in the space back of the cathode and would form the central bright patch. On the whole, then, it seems established within the limits of error of the experiment that alpha particles were given off from the anode and formed an important part of the *Kanalstrahlen*.

This explanation will also account for the sometimes unaccountable appearance of helium in vacuum tubes through which an electric charge has been passed. A striking example of this is given by Soddy in *Proc. Roy. Soc., London* (*A*), **80**, 94, and while the explanation which he there offers may be the correct one it seems not impossible that the one here suggested may be the true one, instead.

STANFORD UNIVERSITY.

THE OXIDATION OF HYDRAZINE. V. REACTION BETWEEN POTASSIUM IODATE AND HYDRAZINE SULFATE.[1]

BY C. F. HALE AND H. W. REDFIELD.

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The most characteristic of the chemical properties of hydrazine is its vigorous reducing action. This behavior has led to the suggestion of several oxidimetric methods for use in the determination of hydrazine in its inorganic compounds. Among the oxidizing agents that have been employed are ammonium metavanadate,[2] potassium permanganate in acid[3] or in alkaline[4] solution, ammonium and potassium persulfates,[5] Fehling's solution,[6] ammoniacal cupric sulfate,[7] mercuric chloride,[8]

[1] For the earlier articles of this series see Browne and Shetterly, THIS JOURNAL, 29, 1305–12 (1907); 30, 53–63 (1908); 31, 221–37 (1909); 31, 783–99 (1909).

[2] Hofmann and Küspert, *Ber.*, 31, 64–7 (1897). See THIS JOURNAL, 29, 1305 (1907).

[3] Petersen, *Z. anorg. Chem.*, 5, 1 (1893); Roberto and Roncali, *l'Industria chimica*, 6, 178 (1904); *Chem. Zentralbl.*, 1904, II, 616; Medri, *Gazz. chim. ital.*, 36, I, 373–8; *Chem. Zentralbl.*, 1906, II, 459. See also THIS JOURNAL, 31, 226 (1909).

[4] Sabanejeff, *Z. anorg. Chem.*, 17, 480 (1898); 20, 21 (1899). See also THIS JOURNAL, 31, 230 (1909).

[5] Pannain, *Gazz. chim. ital.*, 34, I, 500–4 (1904); Rimini, *Atti accad. Lincei*, [5] 15, II, 320–25; *Chem. Zentralbl.*, 1906, II, 1663. See also THIS JOURNAL, 31, 222 (1909).

[6] Petersen, *Loc. cit.* See also THIS JOURNAL, 31, 787 (1909).

[7] Ebler, *Z. anorg. Chem.*, 47, 371–6 (1905).

[8] Rimini, *Atti accad. Lincei*, [5] 12, II, 376–81 (1903); 15, II, 320–5 (1906); *Chem. Zentralbl.*, 1904, I, 213; 1906, II, 1662. Ebler, *Z. anorg. Chem.*, 47, 377–85 (1905). See also THIS JOURNAL, 31, 790 (1909).

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iodine,[1] and potassium iodate.[2]

The complete oxidation of hydrazine may be expressed by the equation

$$N_2H_4 + 2O = N_2 + 2H_2O.$$

It has been shown in this laboratory[3] that several oxidizing agents that have been employed in the determination of hydrazine either by an oxidimetric or by a nitrometric method fail, under certain conditions, at least, to oxidize hydrazine completely to nitrogen and water, yielding varying amounts of ammonia and hydronitric acid, in accordance with one or both of the equations:

$$2N_2H_4 + O = N_2 + 2NH_3 + H_2O$$

$$2N_2H_4 + 2O = NH_3 + HN_3 + 2H_2O$$

The selection of an oxidizing agent entirely suitable for use in the determination of hydrazine has long been a matter of considerable interest in this laboratory, because of the frequent necessity for numerous determinations of this substance in connection with researches now completed or still in progress. Naturally, the choice was limited to those substances which had been observed to yield, under ordinary conditions, neither ammonia nor hydronitric acid when allowed to act upon hydrazine. Among these substances are potassium iodate and iodine. Complete reliance could scarcely be placed upon either of these substances, however, until the merely negative evidence of its inability to yield ammonia or hydronitric acid had been supplemented by positive proof of its ability to oxidize hydrazine quantitatively to nitrogen and water.

The importance of bearing in mind the behavior of iodine toward hydrazine before deciding upon potassium iodate as a thoroughly reliable substance for use in the determination of hydrazine is apparent from the results obtained in an earlier research conducted in this laboratory.[4] When potassium iodate was allowed to act upon hydrazine sulfate in acid solution and in the presence of silver sulfate, which served to prevent the liberation of iodine, very appreciable amounts of ammonia and hydronitric acid were formed. It seems probable, therefore, that potassium iodate owes its apparent ability to oxidize hydrazine completely to nitrogen and water to the iodine set free during the course of the reaction.

[1] Curtius and Schulz, *J. prakt. Chem.*, [2] 42, 521–49 (1890); Stollé, *Ibid.*, 66, 332–8 (1902); Rupp, *Ibid.*, 67, 140–2 (1903). See also THIS JOURNAL, 30, 60 (1908).

[2] Rimini, *Gazz. chim. ital.*, 29, I, 265–9 (1899); *Atti accad. Lincei*, [5] 15, II, 320; *Chem. Zentralbl.*, 1906, II, 1662. See also THIS JOURNAL, 30, 59 and 62 (1908). Baxter and Tilley, THIS JOURNAL, 31, 201–21 (1909), have employed hydrazine hydrate in the reduction of the iodic acid used in determining the atomic weights of silver and iodine. See also Riegler, *Z. anal. Chem.*, 40, 92–4 (1901); 41, 413–19 (1902); 46, 315–18 (1907); and Schlötter, *Z. anorg. Chem.*, 37, 172–6 (1903).

[3] Browne and Shetterly, *Loc. cit.*

[4] THIS JOURNAL, 30, 62 (1908).

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Rimini[1] has shown that the reaction between potassium iodate in excess and hydrazine sulfate in the presence of sulfuric acid may be expressed by the equation

$$5N_2H_4.H_2SO_4 + 4KIO_3 = 5N_2 + 12H_2O + 2K_2SO_4 + 3H_2SO_4 + 2I_2.$$

He submits no analytical data, however, nor does he describe the exact procedure to be followed in carrying out the analysis. Possibly for these reasons the Rimini method has not enjoyed the wide application that would seem to be justified by its convenience and accuracy.

The purpose of the experimental work to be described in the following paragraphs has been to subject the Rimini potassium iodate method for the determination of hydrazine to a rigorous experimental test. Three series of experiments have been performed. In the first, a number of simultaneous oxidimetric and nitrometric determinations have been carried out, the reaction having been allowed in each case to take place in a current of pure carbon dioxide. In the second series the procedure was similar to that of the first except that the reaction took place in a current of steam. In the third, the oxidimetric method alone was studied under ordinary laboratory conditions.

Materials Used in the Experiments.—The purity of the hydrazine sulfate (obtained from Kahlbaum, Berlin) used in the first two series was tested by the determination of sulfur in six different samples of the material. The average of the six closely agreeing results was 24.57 per cent. Theory for S in $N_2H_4.H_2SO_4$, 24.64 per cent. In the first and second series two potassium iodate solutions were employed having the respective concentrations 7.07 grams and 14.13 grams per liter. The former was used for small samples weighing 0.22 gram or less, and the latter for the larger samples. In effecting the standardization of these solutions the usual procedure was followed. This consists in the reduction of a measured volume of the iodate solution by means of a slight excess of a 10 per cent. solution of potassium iodide, in the presence of dilute sulfuric acid, and subsequent titration of the resulting solution against standard thiosulfate. The latter solution was in turn standardized against twice resublimed iodine. The thiosulfate was added in slight excess, and the blue color of the starch indicator was restored by an iodine solution of which the strength in terms of the thiosulfate solution was known.

Apparatus Used in the Experiments.—In the first two series of experiments a nitrometer not very different from that used by Petersen[2] in his study of the action of boiling hot Fehling's solution upon hydrazine salts, or from the modified Schultze and Tiemann apparatus employed by Purgotti[3] in his investigation of the behavior of certain oxidizing agents

[1] *Loc. cit.*
[2] *Z. anorg. Chem.*, 5, 1 (1893).
[3] *Gazz. chim. ital.*, 26, II, 559 (1896); *Chem. Zentralbl.*, 1897, I, 487.

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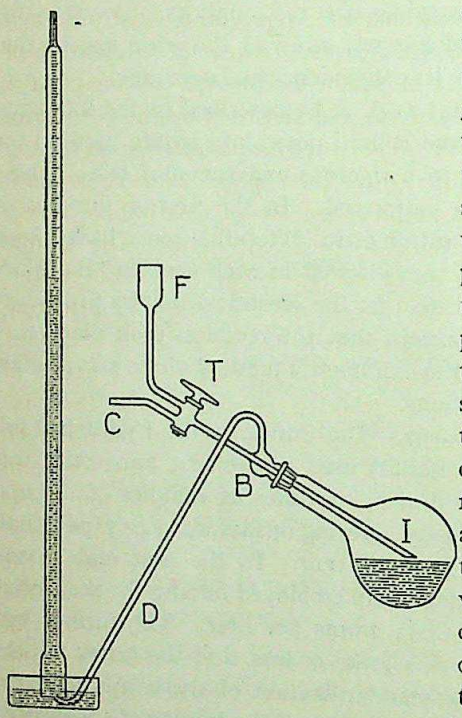
toward hydrazine, was employed. The essential parts of this apparatus are shown in the accompanying sketch. From the fact that iodine is abundantly liberated during the course of the reaction to be studied arose the necessity that the apparatus should be constructed entirely of glass. An ordinary 500 cc. glass stoppered wash bottle was modified by fusing on the two-way stopcock T, and the delivery tube D. The measuring tube consisted of a Hempel gas buret, to the lower end of which had been sealed a short tube of larger diameter, which served to prevent loss of gas when a rapid current was being passed through D. The funnel tube F served to admit the sample of hydrazine sulfate, and the tube C was used, in the first series, for establishing connection with an apparatus for generating pure carbon dioxide, modeled after that of Bradley and Hale.[1] The connection at this point was rendered impervious to air by means of a mercury seal. During the progress of the experiments the evolution flask was inclined at such an angle that no gas trap was formed either in the flask itself or in the bulb B. Both the stopper and the stopcock were found to be gas-tight under all pressures to which the flask was subjected. Inasmuch as the pressure in the flask during the experiments varied but slightly, if at all, from that of the atmosphere it was considered sufficient to test the apparatus at pressures from 23 cm. of mercury below atmospheric, to 27 cm. above atmospheric pressure. The nitrometer tube was filled with a concentrated solution of potassium hydroxide (3 : 2) at the beginning of each experiment in the first series, and with water in the second series. For heating the evolution flask, a bath of strong calcium chloride solution was found to be very convenient.



Action of Potassium Iodate upon Hydrazine Sulfate in an Atmosphere of Pure Carbon Dioxide.—In each of the six experiments of the first series a volume of the potassium iodate solution from 2–5 cc. in excess of the

[1] THIS JOURNAL, 30, 1090–6 (1908).

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amount theoretically required for the complete oxidation of the hydrazine sample was introduced into the evolution flask and was diluted to about 200 cc. After connection with the carbon dioxide generator had been established, the stopcock T was adjusted to permit the current of gas to pass through the flask, and out through the delivery tube into the room. The solution in the flask was boiled for ten minutes and was then allowed to cool in a current of carbon dioxide. When the circulation of the gas had continued for an hour, a half-hour sample was collected in the nitrometer, and the residual bubble of gas, not absorbed by the potassium hydroxide solution, was drawn off into a narrow tube mounted upon the top of a Hempel gas burette and provided with a stopcock at its upper end. Measured under atmospheric pressure, the volume of this bubble rarely amounted to more than a few tenths of a cubic centimeter. The sample of hydrazine sulfate, dissolved in 25 cc. of previously boiled hot water, was introduced into the flask from the funnel tube F by suitably adjusting the stopcock T. The container and the funnel tube were rinsed with four successive 25 cc. portions of hot water. At this point the current of carbon dioxide was diverted from the flask by closing T, and the contents of the flask were boiled until the liberated iodine had been driven off. As a rule it was found necessary to continue the boiling for from twenty to thirty minutes in order to insure the complete expulsion of the iodine. That the prolonged boiling effected also the removal of all evolved nitrogen from the flask was evident from the fact that on renewing the carbon dioxide circulation practically all of the gas issuing from the delivery tube was absorbed before the bubbles reached the meniscus of the potassium hydroxide solution in the nitrometer. To insure the complete transfer of the nitrogen, however, a current of carbon dioxide was sent through the apparatus for fifteen minutes after the boiling was discontinued. In order to permit correction of the volume of nitrogen for the small volume of unabsorbable gas present in the carbon dioxide, care was of course taken to keep the speed of the gas constant throughout each experiment, and to record the exact length of time that the gas was used. At the expiration of the fifteen minutes the delivery tube was removed from the absorbing solution, and the current of carbon dioxide cut off. The flask was then allowed to cool to room temperature. After the solution had been shown, by means of the starch test, to be free from uncombined iodine, the excess of potassium iodate was determined by the method already indicated in connection with the standardization of the solution.

The nitrogen was drawn from the nitrometer into a Hempel simple mercury pipet[1] containing 10 cc. of potassium hydroxide solution, and thence into a water-jacketed Hempel gas buret, in which mercury was used as the confining liquid, where the volume was accurately measured.

[1] Hempel-Dennis, "Methods of Gas Analysis," 1902, p. 67.

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It was next introduced into a pipet containing 10 cc. of alkaline pyrogallol, and was then transferred to the buret for final measurement. Both reagents had previously been saturated with nitrogen, as well as the small volume of pure water (about 1 cc.) introduced into the buret to insure saturation of the gas with aqueous vapor. The final volume was thus virtually measured over water, and a correction for the tension of aqueous vapor was consequently introduced in calculating the volume of the gas at 760 mm. and 0°.

Small amounts of oxygen, varying in different experiments from 0.2–0.5 cc., were always found. The proper manner of introducing a correction for the nitrogen, which undoubtedly accompanied this volume of oxygen, was at first by no means obvious. To be sure, a very small amount of air was admitted as an impurity in the carbon dioxide. The correction for this volume would be, clearly, four-fifths of the residue unabsorbed by potassium hydroxide in the half-hour test run, apportioned for the time during which the carbon dioxide current was passing through the apparatus after the collection of the nitrogen had begun. This correction, however, did not account for all of the oxygen found. Another source from which small volumes of oxygen and nitrogen could be introduced into the apparatus was to be found in the solutions employed. Obviously the error due to this source could be estimated by dispensing with the carbon dioxide, as has been done in the second series of experiments. The only other source of air considered was the absorbing solution in the nitrometer. This solution was always boiled immediately before each experiment and was kept hot by the steam escaping from the delivery tube. The possible error due to the diffusion out of oxygen remaining in the absorbing solution was assumed to be negligible. These considerations and the results of experiments in which no carbon dioxide was used, led to a correction for air dissolved in the solutions introduced into the flask. For this correction recourse was had to the work of Petterson and Sonden[1] and a correction amounting to twice the volume of oxygen found was applied in all cases.

The results obtained in the experiments in which a current of carbon dioxide was employed are given in Table I.

The percentages of hydrazine have been calculated oxidimetrically—that is, on the basis of the iodate used. These results clearly indicate that the hydrazine is oxidized quantitatively under the described conditions to water and nitrogen. It was considered wise, however, as an additional precaution, to test the residual solutions for ammonia after the titrations had been completed. To carry out this test, the solutions were made strongly alkaline with solid potassium hydroxide and one-quarter of the liquid was in each case distilled off into standard acid. After the

[1] *Ber.*, 22, 1443 (1889).

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acid had been titrated, the solution was again made alkaline and Nessler's reagent was added. The titration of the acid was in every case well within the limits of experimental error, and the test with Nessler's reagent was no more pronounced than could be obtained with an equal volume of distilled water to which the same amounts of the various solutions used had been added.

TABLE I.

Number of experiment.	$N_2H_4.H_2SO_4$ used. Gram.	Hydrogen found. Gram.	Hydrogen found. Per cent.	Per cent. N_2H_4.	Nitrogen found. Corrected volume. cc.	Nitrogen found. Weight. Gram.	Nitrogen found. Per cent.
1.....	0.1183	0.00367	3.10	24.64	20.4	0.0255	21.49
2.....	0.2088	0.00645	3.09	24.56	35.9	0.0448	21.48
3.....	0.2100	0.00648	3.09	24.54	36.6	0.0458	21.79
4.....	0.2099	0.00647	3.08	24.50	36.2	0.0452	21.54
5.....	0.2014	0.00622	3.09	24.55	35.1	0.0439	21.80
6.....	0.2044	0.00632	3.10	24.59	35.1	0.0439	21.46
Average.....			3.09	24.56			21.59
Theory.....				24.63			21.53

Action of Potassium Iodate upon Hydrazine Sulfate at 100° in an Atmosphere of Steam.—The only change in the apparatus already described was the replacing of the inner tube I with a capillary tube which was bent downward so that it reached the bottom of the flask when the apparatus was set up as shown in the figure. The lower end of this tube was drawn out to a small diameter in order that the solution of the sample could be admitted in a thin stream below the surface of the oxidizing solution. It was the practice to fill this tube with hot boiled water just before attaching the flask. The iodate solution was then boiled for twenty minutes to expel the air in the flask and delivery tube. The sample was slowly introduced as in the first series of experiments, and the boiling was continued until the iodine had been entirely driven off. It was clearly evident that the evolution of nitrogen had ceased and that the gas had all been swept over into the nitrometer long before the iodine color disappeared. The solution, cooled to room temperature, was tested for the free iodine and was titrated in the manner already outlined. The average amount of oxygen present in the nitrometer gas was the same as in the first series, although no oxygen at all was found in the third experiment.

In Table II will be found the results of the series of experiments in which no carbon dioxide was used.

A comparison of the results obtained in the two series of experiments shows that those of the second series are not quite so closely in accord with theory as are those of the first series. That this difference is attributable to experimental error that is not readily avoidable in the second series, rather than to any change in the reaction when the sample is added

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to boiling iodate solution, seems evident. A change in the reaction in the direction of incomplete oxidation would be accompanied by a shrinkage in the amount of nitrogen and it is plain that any oxidation of nitrogen, that is ultra-oxidation of hydrazine, would have the effect of raising the percentage of hydrazine found. Tests for ammonia were made as in the earlier experiments with the same negative results.

TABLE II.

Number of experiment.	$N_2H_4 H_2SO_4$ used Gram.	Hydrogen found. Gram	Hydrogen found. Per cent.	Per cent N_2H_4	Nitrogen found. Corrected volume cc.	Nitrogen found. Weight. Gram.	Nitrogen found. Per cent.
1.....	0.2184	0.00674	3.09	24.54	38.1	0.0475	21.77
2.....	0.2124	0.00654	3.08	24.48	36.8	0.0460	21.68
3.....	0.2135	0.00659	3.09	24.54	36.9	0.0461	21.60
4.....	0.4138	0.01277	3.09	24.53	71.0	0.0888	21.47
5.....	0.4190	0.01292	3.08	24.52	72.5	0.0907	21.64
6.....	0.3365	0.01120	3.08	24.47	62.4	0.0781	21.53
Average.....			3.09	24.51			21.61
Theory.....				24.63			21.53

It is obvious that a further change in the method of introducing the sample might be made. By a cradle-like arrangement on the upper side of the inner tube I (Fig. 1), the weighed sample, contained in a small test tube, could be placed inside the flask at the beginning of the experiment. After the requisit preliminary boiling the test tube could be dislodged by a slight jarring of the apparatus. This method would obviate the introduction of 125 cc. of water with the sample, the air in the test tube being displaced by a few cubic centimeters of water before putting the tube into the cradle. On attempting to employ this method it was found that the reaction was too violent when the solid hydrazine sulfate was suddenly thrown into the boiling iodate solution. Some of the nitrogen was carried out under the nitrometer in the early stages of the reaction. This difficulty was not entirely overcome by immersing the mouth of the nitrometer under a few centimeters of mercury. It became evident that these experiments could contribute nothing to the present purpose, and after a few trials they were abandoned.

Study of the Rimini Method under Ordinary Conditions.—The results of the simultaneous oxidimetric and nitrometric determinations carried out in the two preceding series of experiments demonstrate that within the limits of experimental error, the reaction between potassium iodate and hydrazine sulfate takes place in accordance with the equation given by Rimini. The only remaining step, then, in the complete vindication of the Rimini method as a reliable means of determining hydrazine consists in a test of the method under ordinary laboratory conditions.

The hydrazine sulfate used in this third series of experiments was ob-

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tained from Raschig, and was marked 100 per cent. pure. One kilogram of this material was dissolved in water, and the solution was evaporated until crystallization started. The hot solution was then filtered and the filtrate was thoroughly agitated by means of mechanical stirrers until it had cooled to room temperature. The crystals were filtered upon a Buchner funnel, were washed with 10 liters of cold distilled water, and were dried for ten hours in an air bath at 110°. This product was shown by titration with tenth-normal sodium hydroxide to be slightly deficient in sulfuric acid. It was consequently recrystallized from dilute sulfuric acid by the method just described, with the result that a product of entirely satisfactory composition was obtained. The solution of hydrazine sulfate used in the experiments contained 5.4000 grams of the salt per liter. The potassium iodate solution contained 7.1045 grams per liter, and was consequently of such strength that 1 cc. was equivalent to 1 cc. of the hydrazine sulfate solution. The sodium thiosulfate solution was standardized very carefully against solutions of resublimed iodine, and of potassium dichromate, and was made exactly tenth-normal.

The details of a series of ten experiments are summarized in Table III.

TABLE III.

Number of experiment.	Cc. of hydrazine sulfate solution used.	Cc. of potassium iodate solution added.	Calculated excess of potassium iodate solution in cc.	Cc. water added.	Grams of potassium iodide added.	Cc. 1:4 sulfuric acid added.	Cc. tenth normal sodium thiosulfate required.	Cc. excess of potassium iodate solution calculated from sodium thiosulfate required.	Cc. of potassium iodate solution used up by hydrazine sulfate taken.	Equivalent in grams of hydrazine	Percentage of hydrazine in hydrazine sulfate.
1	20.0	25.0	5.0	155.0	1.0	15.0	10.10	5.07	19.93	0.0265	24.54
2	20.0	30.0	10.0	150.0	2.0	25.0	19.85	9.97	20.03	0.0266	24.67
3	30.0	35.0	5.0	135.0	1.0	15.0	9.95	5.00	30.00	0.0399	24.63
4	30.0	40.0	10.0	130.0	2.0	25.0	19.95	10.01	29.99	0.0398	24.56
5	40.0	45.0	5.0	115.0	1.0	15.0	10.00	5.02	39.98	0.0532	24.62
6	40.0	50.0	10.0	110.0	2.0	25.0	19.90	9.99	40.01	0.0532	24.64
7	50.0	55.0	5.0	95.0	1.0	15.0	9.90	4.97	50.03	0.0665	24.64
8	50.0	60.0	10.0	90.0	2.0	25.0	19.85	9.97	50.03	0.0665	24.64
9	60.0	65.0	5.0	75.0	1.0	15.0	10.00	5.02	59.98	0.0798	24.62
10	60.0	70.0	10.0	70.0	2.0	25.0	20.00	10.04	59.96	0.0798	24.61
Average											24.617
Theory											24.629

The results of these experiments indicate very clearly that the Rimini method is sufficiently accurate for all ordinary purposes, and show that the oxidimetric method is more satisfactory than the nitrometric method for work in which considerable accuracy is required.

The exact procedure to be recommended in carrying out the Rimini method is briefly as follows:

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Weigh out about 0.3 gram of the hydrazine salt or of the solid substance in which the percentage of hydrazine is to be determined and dissolve if possible in about 50 cc. of distilled water. Transfer to a 300 cc. tall narrow-mouthed Erlenmeyer flask and add such a carefully measured amount of potassium iodate solution (containing about 7.1045 grams to the liter) as will give from 5–10 cc. excess of the iodate. (This will be from 60–65 cc., if hydrazine sulfate is being analyzed.) Then add sufficient distilled water to bring the volume up to 200 cc., and boil over a free flame for thirty minutes. During the boiling, the volume will be reduced to about 100 cc. Cool the solution to about 20° and add from 1–2 grams of potassium iodide (free from iodate), to decompose completely the excess of potassium iodate and also to dissolve the iodine that is liberated. After having added about 20 cc. of 1 : 4 sulfuric acid, titrate the solution immediately with 0.1 *N* sodium thiosulfate until a straw-yellow color is reached. Now add 1 cc. of starch solution[1] (previously made by boiling 1 gram of starch with 200 cc. of distilled water for ten minutes, cooling, allowing to settle and decanting off the clear solution) and titrate to disappearance of the blue color.

Summary.

The principal results obtained in the present investigation may be summarized as follows:

1. The oxidation of hydrazine sulfate by potassium iodate has been shown by simultaneous oxidimetric and nitrometric determinations to proceed quantitatively in accordance with the Rimini equation

$$5N_2H_4.H_2SO_4 + 4KIO_3 = 5N_2 + 12H_2O + 2K_2SO_4 + 3H_2SO_4 + 2I_2.$$

2. The reaction is the same whether the hydrazine is added to the potassium iodate in the cold (in an atmosphere of carbon dioxide) or at the boiling temperature (in an atmosphere of steam).

3. Under ordinary laboratory conditions the oxidimetric procedure, essentially as recommended by Rimini, affords an accurate method for the determination of hydrazine.

The chief disadvantage of the method lies in the length of time (thirty minutes) required for the expulsion of the liberated iodine. In a future communication attention will be given to several other methods for the determination of hydrazine.

The present investigation was undertaken at the suggestion of Professor A. W. Browne, and was carried out under his supervision.

CORNELL UNIVERSITY, ITHACA, N. Y.

[1] Mr. Welsh, of this laboratory, reports that under certain conditions methylene blue is preferable to starch as an indicator in this titration. See F. S. Sinnatt, *Analyst*, 35, 309 (1910).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

EUROPIUM.

BY C. JAMES AND J. E. ROBINSON.

Received June 21, 1911.

By fractionally crystallizing the nitrates of a mixture of the rare earths, very rich in samarium and gadolinium, from concentrated nitric acid, Demarçay[1] obtained a new nitrate more soluble than gadolinium and less soluble than samarium. This element, which differed from all the rare earths by its characteristic spectrum, he provisionally named Σ.

In 1900[2] the discoverer obtained this earth in a purer condition and found that the oxide was white, with a pink tinge. The salts were of a pale rose color and gave the following absorption spectrum: 590, 570, 535, 525, 465, 395.5, 385.5, 380.5. None of these bands were strong, however. A year later Demarçay[3] obtained the element in a fairly pure condition and named it europium. He also found that the crystallization of the double magnesium nitrate gave a more rapid separation.

Some years previous to Demarçay's work, Lecoq de Boisbaudran[4] had observed three lines in certain samarium solutions, which did not occur in Cleve's pure material. These lines were later found to coincide with those given by europium. Crookes, in 1885, discovered the phosphorescent spectrum of europium, and gave the element the provisional name Sub.

Urbain and Lacombe[5] showed that isomorphous bismuth magnesium nitrate came between samarium and europium with regard to its solubility in fairly strong nitric acid. This method enabled them to obtain several grams of europium, in a very pure condition from a comparatively large amount of samarium and gadolinium (610 grams oxides).

In order to obtain a sufficient quantity of this earth for further study, the writers worked up very large amounts of material. This material comprised the following: oxides from insoluble double sodium sulfates from about 200 kilograms of yttrium minerals; all the samarium and gadolinium oxides derived from about 200 kilograms of Brazilian monazite; and about 110 kilograms of oxides obtained from the more soluble double potassium sulfates coming from very large amounts of Carolina monazite.

These crude oxides were first converted into double magnesium nitrates in the following manner: concentrated nitric acid and the oxides were gradually mixed in a large porcelain dish, care being taken not to allow the liquid to become alkaline. All cerium in the ceric condition was reduced by addition of rare earth oxalates of similar metallic content to

[1] *Compt. rend.*, 122, 728.
[2] *Ibid.*, 130, No. 22.
[3] *Ibid.*, 132, No. 24.
[4] *Ibid.*, 114, 575.
[5] *Ibid.*, 138, 628.

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the oxides. About two bottles of concentrated nitric acid were used in each batch. The solution was finally made as nearly neutral as possible, poured into a large earthenware vessel and allowed to stand until it became clear. This operation took about twelve hours. An equal amount of acid was neutralized with crude magnesium oxide. The magnesium nitrate solution was made slightly basic by heating with a little more of the oxide. The precipitate of iron and aluminium hydroxides was then filtered off. The filtrate was acidified and mixed with the rare earth nitrate solution. The mixed liquids were evaporated until such a concentration was obtained that half of the material separated out in a crystallin state upon cooling. The mother liquor was poured off and evaporated further. The double nitrates that separated were recrystallized three times, after which they were drained and placed aside. When the mother liquors began to crystallize badly, owing to increase in the impurities, they were diluted and precipitated with oxalic acid. The oxalates were filtered off on large Büchner funnels, thoroughly washed with water and ignited in fire-clay crucibles placed in a large furnace.

The oxides obtained in the above manner contained small quantities of lanthanum, cerium and praseodymium, large quantities of neodymium and fair amounts of samarium, gadolinium and yttrium earths. This material was converted into the double magnesium nitrate in a similar way, as described above, with the exception that pure magnesium oxide was used. These double magnesium nitrates were fractionally crystallized according to the usual method with 30 per cent. nitric acid as the solvent. After the crystallization had proceeded for a short time, it was found that the neodymium, lanthanum, cerium and praseodymium rapidly collected in the least soluble portion. The intermediate fractions consisted chiefly of the pale yellow samarium compound while the most soluble portions were rich in gadolinium and were colored very pale pink by the erbium metals. As soon as the crystals of the simple nitrates of the yttrium elements made their appearance, it was deemed advisable to commence the addition of the isomorphous bismuth magnesium nitrate. Five kilograms of bismuth were converted into the double nitrate. This salt was added in portions of about 1 kilogram to the most soluble fraction, such procedure rapidly eliminating all traces of samarium and europium. When the yttrium earths were entirely freed from samarium and europium they were separated from the series.

With regard to the yttrium earths, it was found that erbium and yttrium separated first, holmium next and lastly dysprosium and terbium. It proved to be practically impossible to free gadolinium entirely from terbium by the magnesium nitrate method. A crystallization of the simple nitrates caused yttrium, erbium, holmium, and dysprosium to pass rapidly into the most soluble part.

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The fractions containing lanthanum, cerium, praseodymium and neodymium were set aside as soon as they were freed from all traces of samarium. Samarium was gradually removed after a large number of crystallizations, at which time it was considered certain that all europium had passed further along the series.

These operations were carried out in very large porcelain dishes. As these dishes were uncovered the top crystals deliquesced, causing the samarium to pass beyond its correct position in the series. Because of this difficulty and since the fractions had decreased in bulk considerably, the series was removed from the dishes and placed in casseroles, which were covered with large watch-glasses. From now on the solvent used was nitric acid of about 50 per cent. concentration. Hitherto the only visible sign of europium was a fine sharp absorption band in the blue, shown by the gadolinium fractions next to samarium.

As the work proceeded, the europium band was observed to become stronger in the fractions between samarium and gadolinium. Later the two bands in the green made their appearance. The fractions kept getting smaller and smaller, since all mother liquors that gave no europium absorption had been removed. At this period nearly all the samarium had been separated. After continuing the work a little longer, the fractions which consisted almost entirely of bismuth magnesium nitrate were mixed according to their absorption spectra. The liquids were diluted, precipitated with hydrogen sulfide and filtered. The filtrate was precipitated with oxalic acid and the europium oxalate filtered off and washed. About 100 grams of this compound were obtained. Each precipitate was then ignited to the oxide, the oxide dissolved in nitric acid, and the resulting solution tested with the spectroscope. The solutions of the europium material nearest to the samarium were found to be still slightly contaminated with that element.

It was decided to submit the whole material to more series of crystallizations. For this purpose it was again converted back to the double magnesium nitrate and mixed with bismuth magnesium nitrate. When the europium was found to be free from samarium, it was dissolved in water, saturated with hydrogen sulfide and the clear filtrate was once again precipitated with oxalic acid. This europium oxalate was then washed, dried and stored for the study of its compounds.

In this work, which required two years, about 30 kilograms of the crude double nitrates of samarium and gadolinium were extracted and fractionated. About 5 kilograms of pure samarium oxalate and about 4 kilograms of nearly pure gadolinium oxalate were prepared.

The authors hope to publish the second part of this paper in the near future.

DURHAM, N. H.

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THE LIQUIDUS SURFACE OF THE TERNARY SYSTEM COMPOSED OF THE NITRATES OF POTASSIUM, SODIUM AND CALCIUM.

By Alan W. C. Menzies and N. N. Dutt.

Received June 26, 1911.

The cases are not yet numerous in which the liquidus surface of a ternary system has been explored throughout the entire range of possible concentration. In many cases where the results promised to be of direct utilitarian value in the arts, portions of such surfaces have been intensively studied, especially in the case of metallic alloys. In the latter case, however, wide regions of concentration fall outside the composition of the commercially useful alloys, and have therefore remained uninvestigated as possessing merely scientific interest. The present work has had its ulterior object in the search for a low-melting bath liquid for use in the laboratory that should, among other qualifications, be stable, transparent, non-volatile, uninflammable, cheap, applicable over wide ranges of temperature, and without harmful action upon glass or metal. Fused nitrates have already been used in this laboratory as elsewhere with some success for this purpose; and, to extend our knowledge of nitrate mixtures in respect of fusibility, one step is here made by a study of the complete liquidus surface for ternary mixtures of the nitrates of potassium, sodium and calcium. It is hoped that further steps in the same direction may be undertaken later.

The Degree of Accuracy Aimed At.—When the temperatures measured are much above 200°, determinations of the freezing and melting points even of ostensibly pure substances by different observers are notoriously discordant. Selecting, for example, as a case in which better concordance might well be expected, the lowest melting of the three components of the system here studied, namely potassium nitrate, we find the melting point of this so well defined and easily purified substance given by the several observers as 339°; 338.3°; 342°; 353° ± 1; 339° ± 2; 320°; 327° (see p. 1375).

In the case of two-component systems, where the solid phase separating on freezing differs in composition from the liquid phase that forms the mother liquor, it is very obvious that such a high degree of concordance cannot be expected as in the case of a single pure substance, for the reason that, in general, the liquid phase varies progressively in concentration as the freezing-out process proceeds. In the presence of still a third component it would seem to be altogether futile to expect the same degree of accuracy in freezing point measurement, especially in view of the added opportunities of error in synthesizing directly the ternary mixtures from materials each of which is a possible contributor of impurity. For the purposes of the study contemplated, therefore, it was considered unprofitable to aim at an accuracy of freezing point measurement higher

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than ± 1°, as this is amply sufficient to adequately characterize the liquidus surface. The proposed degree of accuracy having been thus decided upon in advance, it became possible to avoid the labor of unnecessary and disproportionate refinements in all of the subsequent work. In this, as in other normal cases, higher precision of measurement would be attainable only by the expenditure of much more than a proportional amount of time and labor.

The Material Employed, and Its Purity.—All three nitrates were the purest preparations of Kahlbaum. Qualitative examination demonstrated the absence of chloride, chlorate, perchlorate, sulfate and of heavy metals. Calcium was absent from the potassium and sodium nitrates. The nitrates were then dried. The potassium and sodium nitrates required nothing but grinding and maintaining at 150° until the weight was constant. The calcium nitrate, which contained four molecules of water of hydration, was gradually desiccated by gentle heating and the drying completed at 150° until constant weighings were obtained.

Quantitative examination of each of the three nitrates was made as follows:

Potassium Nitrate.—Quantities of about 5 grams were converted into sulfate in a platinum crucible in the usual way. In the results here tabulated all weights are stated in grams:

	Nitrate taken.	Sulfate found.	Sulfate expected.	Difference.
(1).....	5.1434	4.4298	4.4312	0.0014
(2).....	5.1423	4.4276	4.4303	0.0027

If the difference in the last column is attributed solely to the presence of sodium nitrate, then this impurity is present to the extent of (1) 0.19 per cent.; (2) 0.36 per cent.

An estimate of the effect of impurities upon the melting point may be obtained by a consideration of the "molecular depression" for fused potassium nitrate regarded as a cryoscopic solvent. Using, in van't Hoff's formula, the latent heat of fusion observed by Person,[1] Stern[2] computes for potassium nitrate the molecular depression 16°.

Sodium Nitrate.—The results obtained by a similar treatment were:

	Nitrate taken.	Sulfate found.	Sulfate expected.	Difference.
(1).....	5.1746	3.6759	3.6758	0.0001
(2).....	5.1646	4.6689	3.6688	0.0001

Calcium Nitrate.—Portions of about 2 grams were converted to oxide by ignition in platinum crucibles over the blast-lamp. The following results were obtained:

[1] *Pogg. Ann.*, 10, 300 (1847).
[2] *Z. physik. Chem.*, 65, 667 (1909).

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	Nitrate taken.	Oxide found.	Oxide expected.	Difference.
(1).....	1.9529	0.6654	0.6673	0.0019
(2).....	1.8498	0.6305	0.6322	0.0017

If the difference be attributed to presence of water in the nitrate taken, the amount of this impurity would be (1) 0.09 per cent. and (2) 0.3 per cent., respectively.

An approximate estimate of the effect of impurities on the freezing points of each of the three nitrates may be obtained directly from an inspection of Table I below, from which it may be seen, for example, that the presence of one molecule of sodium nitrate among 99 molecules of potassium nitrate would lower the freezing point of the latter by less than 3°; or that one equivalent of calcium nitrate in 99 equivalents of sodium nitrate would lower its freezing point by about 1°. In view of the degree of accuracy aimed at, therefore, the degree of purity of the materials used may be considered adequate.

The Method Employed.—About 20 grams of each of the mixtures investigated were prepared by synthesis, weighings being made to the nearest centigram. After grinding in a mortar, each mixture was transferred to a 130 × 12 mm. test tube, which was then heated in a suitable bath. After melting was complete, the temperature was slowly lowered, with constant stirring, until the first fine crystals appeared; the temperature was then noted upon a thermometer immersed directly in the melt. By slowly raising the temperature again, the point at which the last crystals vanished was likewise noted. The process could be repeated with concordance within 0.2°, provided the stirring was sufficiently vigorous.

The Heating Bath and Stirrer.—In the earlier experiments, stirred paraffin and other transparent baths were used with success. It was later found, however, that results of adequate accuracy could be much more quickly obtained by the use of an air bath constructed as follows. A glass lamp chimney (250 mm. long, 37 mm. internal diameter) rests on a wire gauze, which is supported by a stoneware tower of the type so often used to protect Bunsen burners from draughts. A chimney was selected whose upper end was broken in such a way as to leave two projecting triangular apices of equal height on opposite sides. A sheet of asbestos (130 mm. square, 7 mm. thick) clamped in a ring stand, by engaging the two apices in two corresponding holes, maintained the chimney in a vertical position and served also to support, by a close-fitting hole, the test tubes containing the nitrate mixtures.

The stirrer consisted of a glass rod (2 mm. diameter) bent in a circle at its lower end so as to loosely embrace the thermometer. A slender cord passing from the top of the stirrer, through a "pulley" formed of a bent glass tube, to a pin set eccentrically in a rotating disc imparted to the

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stirrer a vertical reciprocating motion. The amplitude of this motion could be varied at will by altering the distance of the pin from the axis of the disc, which was driven by a small three-speed electric motor.

The Temperature Measurement.—A nitrogen-filled thermometer of Jena resistance glass 59^{III} and graduated in whole degrees from 180°–550° over a length of 250 mm. was employed throughout, except in the case of two or three of the lowest temperatures which fell below 180°. The ice-point of this thermometer was determined every working day by the help of the short range of graduations for the purpose, with which the thermometer was provided. A perfectly regular and continuous rise of zero was observed amounting in all to 0.2°. No trouble was experienced from distillation of mercury within the stem.

As the depths of the melt contained in the test tube were not greater than 80 mm., it is obvious that complete immersion of the mercury thread in this liquid was not attainable except for the lower temperatures. It is well known that, for temperatures above 300°, correction for "exposed thread" based on the usual method of computation is far from satisfactory. To overcome this difficulty, the thermometer was standardized with the same amount of exposed thread and with other conditions the same as when it was used.

For purposes of standardization a platinum resistance thermometer of the form devised by Haagen was employed. The quartz-embedded platinum wire forming the "bulb" of this thermometer had an electrical resistance at 0° of about 50 ohms. In comparison with this large resistance, changes of resistance in the gold leads connecting the bulb with the head of the thermometer were negligible, where an accuracy of only 0.1° was aimed at. The resistance measurements were made upon a dial-form Wheatstone bridge whose resistance coils had been previously calibrated. With the arrangement employed, the galvanometer used was sufficiently sensitive to indicate fiftieths of a degree over the whole temperature scale.

As standard points of temperature for use in determining the scale of the platinum thermometer were used the boiling points of sulfur (assumed as 445° on the thermodynamic scale) and the boiling and freezing points of water. The ice-water used in obtaining the ice-point of the thermometer left on subsequent evaporation a residue of 1 part in 10,000, an amount which would not vitiate the accuracy to tenth degrees, which was aimed at in this standardization.

The difference formula of Callendar was utilized in the reduction of resistance to temperature. The other precautions observed have been discussed on another occasion.[1]

[1] THIS JOURNAL, 32, 1422 (1910).

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The Mixtures Examined.—In order sufficiently to cover the field, 70 different mixtures, in all, were examined. It was found that about 10 of the mixtures containing the largest proportions of calcium nitrate yielded, on melting, slightly opalescent instead of perfectly clear liquids. The point at which these mixtures began to deposit crystals was therefore somewhat more difficult to determine than in cases where the liquid was entirely clear. With the very flexible heating arrangement described, however, frequent repetition in cases of doubt is an extremely simple matter, while the speed of cooling can be made as slow as desired. In all cases the temperatures recorded are those at which the first separation of crystals became visible in a briskly stirred liquid cooling not faster than 1 degree per minute.

Tabulation of Results.—With a view to subsequent convenient tabulation, the composition of the mixtures synthesized was chosen so as to fall on the crossing points of the triangular diagram shown in Fig. 1. It

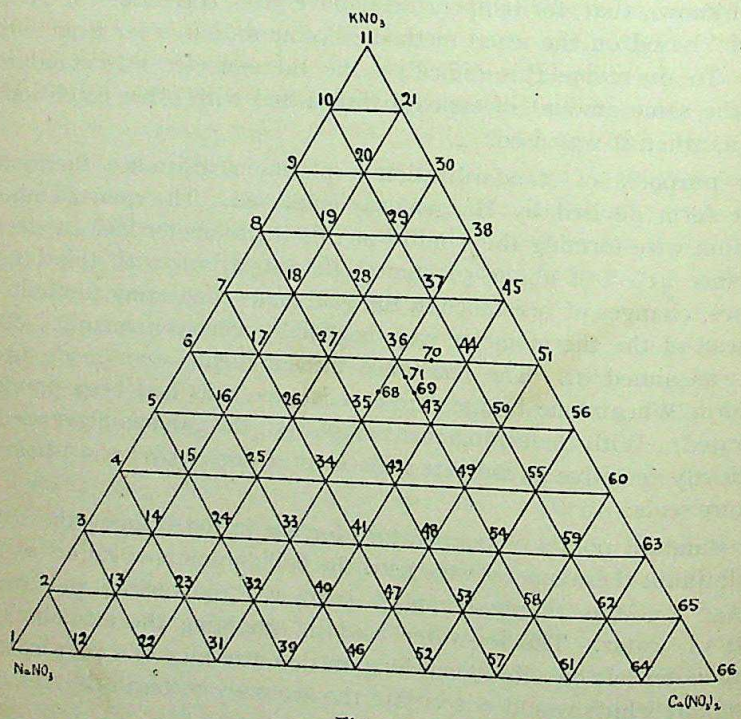

Fig. 1.

will be recalled that in such a diagram each of the three vertices of the triangle represents one of the three chosen substances, considered as 100 per cent. pure. The sum of the three perpendiculars from any selected point within an equilateral triangle upon the three sides is constant and

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may be considered equal to 100. Accordingly, if percentage composition of each component is taken as represented by the length of the perpendicular from the selected point upon the side opposite to the vertex occupied by that component, it is clear that, with a ruled diagram such as Fig. 1, the percentage composition in each of the three components may, for any crossing point, be read off by inspection.

It was considered more rational to represent equivalent percentages rather than percentages by weight of the three components; for example, point number 25 in Fig. 1 represents the composition of a mixture containing the three nitrates in the proportion of 30 equivalents of potassium nitrate (KNO_3), 50 equivalents of sodium nitrate ($NaNO_3$), and 20 equivalents of calcium nitrate $^1/_2[Ca(NO_3)_2]$; in all, one hundred equivalents.

The number of crossing points obtained by a division of the three sides of the triangle into ten parts, as shown, was considered sufficient for the present purpose. A few additional mixtures were studied in the neighborhood of the ternary eutectic.

The adjoining table, in which the number of each mixture refers to a composition which may be read off from Fig. 1, contains the complete record of all freezing points observed. The position of points numbers 67, 68, 70, and 71 is intended to be exactly midway between the neighboring points; the point 69 lies midway between 36 and 43.

TABLE I.

Point No.	Equivalent percentage.			Freezing point.
	$NaNO_3$.	KNO_3.	$\frac{1}{2}[Ca(NO_3)_2]$.	
1	100	0	0	315.1°
2	90	10	0	290.1
3	80	20	0	274.5
4	70	30	0	255.0
5	60	40	0	237.6
6	50	50	0	228.1
7	40	60	0	242.9
8	30	70	0	262.5
9	20	80	0	289.3
10	10	90	0	316.7
11	0	100	0	346.3
12	90	0	10	303.9
13	80	10	10	284.2
14	70	20	10	260.4
15	60	30	10	234.5
16	50	40	10	225.0
17	40	50	10	222.0
18	30	60	10	240.0
19	20	70	10	268.5
20	10	80	10	291.2
21	0	90	10	318.5
22	80	0	20	285.6
23	70	10	20	263.3

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TABLE I—(*Continued*).

Point No.	Equivalent percentage. $NaNO_3$.	KNO_3.	$\frac{1}{2}[Ca(NO_3)_2]$.	Freezing point.
24	60	20	20	240.9°
25	50	30	20	219.8
26	40	40	20	206.3
27	30	50	20	196.2
28	20	60	20	225.0
29	10	70	20	255.0
30	0	80	20	295.2
31	70	0	30	272.9
32	60	10	30	241.0
33	50	20	30	225.0
34	40	30	30	211.6
35	30	40	30	199.3
36	20	50	30	180.0
37	10	60	30	220.7
38	0	70	30	262.2
39	60	0	40	249.8
40	50	10	40	227.0
41	40	20	40	217.2
42	30	30	40	207.6
43	20	40	40	195.2
44	10	50	40	205.3
45	50	60	40	210.5
46	50	0	50	136.5
47	40	10	50	221.5
48	30	20	50	208.7
49	20	30	50	197.8
50	10	40	50	214.8
51	0	0	50	221.9
52	40	0	60	284.1
53	30	10	60	258.2
54	20	20	60	231.2
55	10	30	60	247.8
56	0	40	60	263.3
57	30	0	70	355.4
58	20	10	70	345.3
59	10	20	70	318.3
60	0	30	70	345.3
61	20	0	80	421.0
62	10	10	80	428.0
63	0	20	80	450.0
64	10	0	90	490.0
65	0	10	90	508.4
66	0	0	100	[561.0][1]
67	25	50	25	184.0
68	25	45	30	183.0
69	80	45	35	175.0
70	15	50	35	186.0
71	20	47.5	32.5	176.0

[1] Carnelley. This point was not determined by us.

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The Solid Figure, Its Surfaces, and Its Vertical Sections.—If we agree to represent temperature along an axis perpendicular to the plane of the paper, we have, in Table I, the requisit coördinates in three-dimensional space of 70 points which may be joined smoothly by continuous surfaces. The outlines of vertical sections of these surfaces by three series of planes parallel to the three sides of the triangle were now obtained by direct plotting of the observations. For example, regarding Fig. 1 as a plan, the vertical section on 4–60 should show the curve obtained by plotting the several temperatures observed along 4–60 against the corresponding concentrations. From the sets of curves so obtained, the concentrations could be located graphically at which various mixtures froze at selected round numbers of degrees. By smoothly joining the sets of points representing concentrations of mixtures of identical freezing point the series of isotherms shown in Fig. 2 were obtained. These isotherms are contour lines of the liquidus surface, and are shown for each 10° interval to 300°, and for each 50° interval above that temperature.

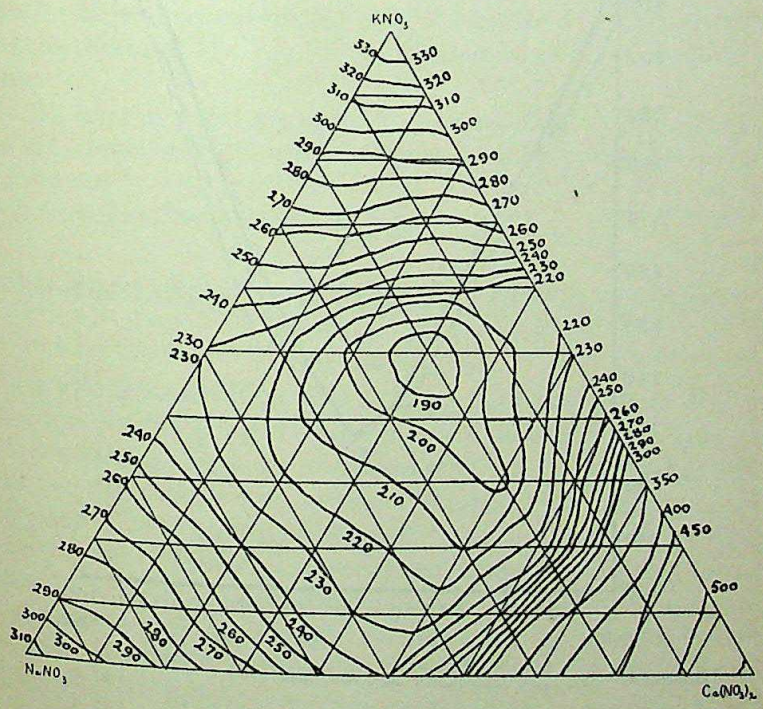

Fig. 2.

Comparison of Values Obtained with those of Other Observers.—The present work overlaps that of others in that, (1) the individual melting points of sodium and potassium nitrates have already been determined by several investigators; (2) points on the freezing point curve of binary

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mixtures of potassium and sodium nitrates have been determined by three observers; (3) one observer[1] determined the freezing point of a single mixture of calcium and sodium nitrates.

The various values obtained are quoted below, but without critical discussion on account of the want of precision in the thermometry of the older measurements. In the case of the comparatively recent measurements of Carveth,[2] however, the thermometers used were compared with what would seem to be thermometers verified at the Reichsanstalt,[3] and the readings were doubtless corrected for exposed thread, zero creep, etc.

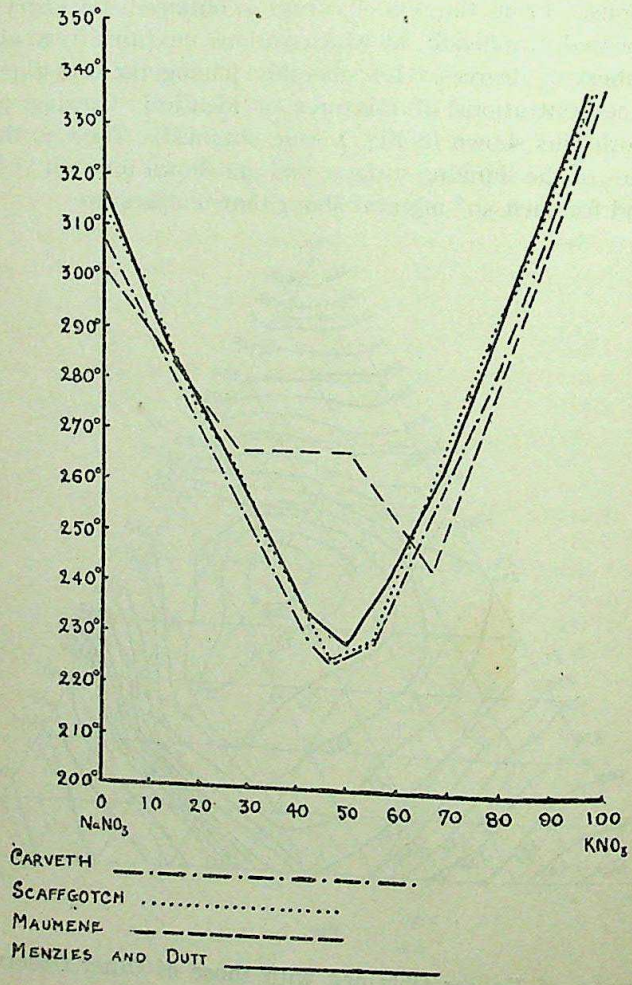

Fig. 3.

[1] Maumené, *Compt. rend.*, 97, 45 (1883).
[2] *J. Physic. Chem.*, 2, 209 (1898).
[3] *Loc. cit.*, p. 211.

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The test tubes containing the melted material were cooled in air at room temperature and were stirred with the thermometer until the first crystals appeared. It is stated that "with the use of such small amounts of material and this method of measurement, there is possibly an error of 2° as a maximum."

For the melting point of sodium nitrate the following values have been obtained: Person (1849), 310.5°; Braum (1875), 342°; Carnelley (1876–78), 319°, 316°, 330° ± 2; Guthrie, 305°; Maumené (1883), 298°; Carveth (1898), 308°. We found 315.1°.

For potassium nitrate, the following are the melting points obtained by others: Person, 339°; Schaffgotsch (1857), 338.3°; Braum, 342°; Carnelley, 353° ± 1, 332° ± 5, 339° ± 2; Guthrie, 320°; Maumené, 327°; Carveth, 337°. We found 346.3°.

For the freezing point curve for binary mixtures of potassium and sodium nitrates, the four curves shown in Fig. 3 embody the results obtained by Schaffgotsch,[1] Maumené, Carveth and ourselves. Percentage by weight is represented on the axis of abscissas. The usual large discrepancies between the results of different observers are here again in evidence.

For the freezing point of the mixture represented by [$NaNO_3$, $Ca(NO_3)_2$], Maumené obtained 235°. Interpolation on the appropriate curve would lead us to 261°.

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THE MECHANICAL STIMULUS TO CRYSTALLIZATION. II.

BY S. W. YOUNG AND R. J. CROSS.

Received June 5, 1911.

In a previous paper[2] by one of us it has been pointed out that mechanical impacts produced within supercooled liquids and solutions are capable of stimulating these to crystallization, and that further, the sensitiveness of the supercooled system increases with the degree of supercooling, and that to stimulate crystallization in very slightly supercooled systems requires very large mechanical stimulus. It was also pointed out that there seems to be no justification for dividing the supercooled field into metastable and labil fields as the whole supercooled field appears to be labil in such a sense that crystallization may be forced at any point within it by sufficient mechanical stimulus.

It has long been held that foreign particles, such as dust and the like, exert under some circumstances an influence upon the production of crystals in supercooled liquids. No very definit ideas concerning the influence of such particles have been advanced up to the present time,

[1] *Pogg. Ann.*, 102, 293 (1857).

[2] THIS JOURNAL, 33, 148.

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so that on account of the vague and speculative character of the many references to be found in the literature, it seems hardly necessary to cite them here.

The following investigation was taken up for the purpose of throwing some light upon the question. Two points of view are possible:

1. That the effect of foreign particles is entirely a kinetic one, and that the stimulus which they offer to crystallization is of an entirely mechanical character, and depends upon the production of a mechanical disturbance when two such particles come into impact with one another, or perhaps when one of them comes into impact with the walls of the containing vessel.

2. That the effect of the foreign particles is at least in part of some other nature, not at present definable.

In the investigation to be described the arbitrary assumption was made that the effect of the particles is purely kinetic. Upon the basis of this assumption certain quite definit predictions could be made as to the conduct of supercooled liquids carrying known numbers of particles of known size, and moving at a known rate. It must, however, be stated at the outset that so many factors enter into the determination of the rate of motion of a particle within a liquid when the latter is in a state of agitation (as being stirred by a stream of gas) that such predictions cannot possibly be of more than a roughly qualitative character.

The more important points upon which such predictions may be made are the following:

1. *The Effect of the Mass of the Particles.*—If the effect of the particles is purely kinetic, the disturbance which would be produced by impact between two particles of the same size would be proportional to their masses. Thus at a given velocity of agitation, and other factors remaining constant, a liquid charged with particles of large mass should permit of less supercooling than the same liquid charged with particles of small mass.

2. *The Effect of the Number of Particles.*—If but relatively few particles are present in a liquid, the chances of an impact between any two of them occurring within a given interval of time will be relatively small. As the number of particles in a given volume increases, the probability of such an impact occurring in a given interval of time will increase, and as a matter of fact in proportion to the square of the number of particles. Thus in a liquid carrying a small number of particles, and being cooled at a given rate, and at the same time being kept in a constant state of agitation, erratic values for the amount of supercooling observed are to be expected. This will be due to the fact that in one case the impact which causes the crystallization may not occur until after a considerably greater lapse of time than in another case, and as the liquid is

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being continually cooled the observed temperature of crystallization will be considerably lower.

Since when the number of particles increases, the probability of the impact occurring within a given time increases very rapidly, it is to be expected that the results for the supercooling observed will become more nearly constant and at the same time show a somewhat lower average. When the number has increased to such an extent that the impacts succeed one another in very rapid succession, the result should be an approximately constant value for the supercooling, and one which is independent of the number of particles within considerable limits.

When the number of particles become very great the mechanical character of the liquid will become considerably altered, especially when agitated by a gas stream. Under these conditions the liquid will take on more or less of the character of a mud; the successive bubbles of gas will lift greater amounts of the liquid and these will drop back with considerable force into the bulk of the liquid. With liquids in this state it is to be expected that considerably greater impact values may occur than those due to the mere meeting of the individual particles, and consequently less supercooling is to be expected.

3. *The Effect of the Character of the Liquid.*—It is readily seen that certain physical properties of the liquid, especially its viscosity, will play an important part in determining the velocity with which two particles meet within the liquid under the stimulus of a given agitation. This fact, together with the more or less fortuitous character of the agitation produced by a stream of gas, makes it impossible to reach any exact quantitative idea of the impact values produced under the conditions of such experiments. It may be predicted, however, that small particles, owing to the relatively greater surface which they expose, will be more retarded in their motions than will large ones. Hence it is to be expected that in order to reach the constant maximum effect (barring the mud effect), there will be required a considerably greater number of small particles than of large ones.

It may also be foreseen that any influence which increases the viscosity of the liquid will decrease the impact values for all particles, and will affect small to a greater extent than large ones. Thus the addition of a substance such as gelatin to water, which materially increases its viscosity without largely affecting its other physical properties, should to some extent protect the water against the crystallization stimulus of foreign particles, and this effect should be greater for small particles than for large ones.

Experimental Part.

Several forms of apparatus were used in the preliminary experiments. In principle these were all the same. They consisted of a Beckmann

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freezing tube with a two-hole stopper. Through one hole was introduced a thermometer and through the other a tube leading nearly to the bottom, which served to admit the hydrogen gas used to stir the liquid. The particles whose effect was to be investigated were dropped into the liquid. The whole was surrounded by an ammonia cooling bath which produced a rate of cooling of about one-half degree a minute.

A number of preliminary experiments were devoted to studying the effect of the rate of flow of the gas and the form and nature of the aperture through which the gas was admitted. The effect was found to be independent of the material of which the aperture was made, the value for the supercooling being the same for apertures of glass, aluminium and brass. The effect of the rate of flow of the gas was negligible when pure water was used, at least within considerable limits. When foreign particles were present a distinct effect was found, in such a sense that a low rate of flow favored greater supercooling. Increasing the amount of gas and constriction of the aperture both produced the same effect; namely, less supercooling was possible. In order to avoid these effects the same gas tube with a constant flow of gas was used in the following experiments.

A few further preliminary experiments were then made by adding portions of a number of solid powders to the water and observing the temperature of freezing. The distilled water used showed an approximately constant degree of supercooling; namely, —5.7°. The addition of powdered gamboge to this produced an effect so slight as to be practically negligible. Addition of starch gave occasional values as high as —3.0°, and varying from that to the normal value of the water. The results were very erratic, and owing to certain difficulties in its use, the observations were carried no further. Crocus was next tried, and found to give results in the neighborhood of —4°. These were also somewhat erratic, and it was found after a few freezings that the crocus had largely flocculated. Furthermore it showed a marked tendency to adhere to the walls of the tube, whence it was not considered a satisfactory substance to work with. Emery gave much more satisfactory results, but was not altogether free from flocculation and was consequently discarded.

Finally a satisfactory substance was found in the commercial powdered quartz such as is used as a flux in assaying laboratories. This consists of particles of a great variety of sizes, and was found to be nearly free from flocculation, even among the particles of very small sizes. The remainder of the investigation was carried out entirely with this substance, which was first separated into particles of various sizes by methods to be described in the following. The freezing apparatus was also somewhat modified.

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1. *The Method of Separation.*—A first rough separation was made by the method of settling. A considerable quantity of the powdered quartz was stirred up with a large volume of water, and the portions remaining unsettled after respectively one, two and five minutes were decanted off. The portions obtained by such settlement were then brought successively into a flotation apparatus and subjected to further separation. This apparatus consisted of a glass tube of four centimeters diameter and thirty-five centimeters long. The lower end of this tube was drawn down and a small tube soldered on through which a stream of distilled water could be introduced. The upper end was provided with a two-hole rubber stopper, through one hole of which was introduced a thistle tube. Through the other hole was passed a short glass tube which served as the overflow. The separation was carried out as follows: A stream of distilled water was passed through the tube at a constant rate, which rate could be determined by measuring the amount of water passing through in a given time. The partially separated quartz powder mixed with water was then introduced a little at a time and the apparatus allowed to run until no more particles were carried over. By now somewhat increasing the rate of flow of the water, other particles of a somewhat larger size were carried over. If the two rates of flow were not very different, the particles which passed over were of quite uniform size.

By this method four portions of the quartz powder were obtained whose sizes were comparatively uniform in each sample but which differed very considerably in different samples, the intermediate sizes being discarded. These portions will hereafter be characterized as Nos. 1, 2, 3 and 4. No. 1 consisted of such particles as refused to float over when the rate of flow of the water was forty centimeters a minute, but did float over at a water rate of forty-eight centimeters a minute. No. 2 was obtained between rates of flow of 7.7 and 10 centimeters. On account of the great length of time required to obtain appreciable quantities of the finer particles by this method, a somewhat different procedure was used for Nos. 3 and 4. No. 4 was obtained by allowing the separator to run at a rate of 0.4 centimeter a minute. There was thus obtained a sample consisting of particles that would just pass over at that rate, together with particles of all smaller sizes. The sample was freed from smaller particles by repeated settling until under the measuring microscope the particles showed a nearly uniform size. No. 3 was similarly obtained from samples which passed over with the separator running at a rate of 1.2 centimeters a minute.

2. *Determination of the Number of Particles in a Given Volume.*—The four samples thus obtained were brought into known volumes of distilled water, and a count of the number of particles in a cubic centimeter of each was made. For samples 2, 3 and 4 the method used was the

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usual blood count method under the microscope with a Zeiss blood count cell. On account of the settling of the particles it was difficult to obtain a uniform field. This difficulty was obviated by suspending the particles for the purpose of counting in a potassium mercuric iodide solution of the same density as the quartz. In this manner satisfactory results were obtained. In the case of No. 1 the particles were somewhat too large to be accommodated in the blood count cell. They were therefore counted by allowing one cc. of the suspension to flow uniformly from a pipette in drops upon a glass plate. The number of particles in every fifth drop was counted, and the average result was multiplied by the whole number of drops in the one cc. A count of No. 2 was also made by this method, the result checking well with the results for the same sample by the blood count method.

3. *The Diameter of the Particles.*—The diameter of the particles was roughly determined with a measuring microscope. Since the particles were mostly of jagged and irregular shapes these measurements have no very great significance. The results are as follows:

No. 1, 0.10–0.12 mm.; No. 2, 0.03–0.05 mm.; No. 3, 0.012–0.016 mm.; No. 4, 0.008–0.012 mm.

4. *The Mass of the Particles.*—The average mass of the particles in each sample was determined by pipetting off one cc. of each, placing on a weighed watch-glass and allowing the water to evaporate. Dividing the total weight of the particles by the already known number, the average weight of each particle in milligrams was obtained. The results are as follows:

No. 1, 0.002 mg.; No. 2, 0.0005 mg.; No. 3, 0.00002 mg.; No. 4, 0.000007 mg.

Having obtained the above data, each sample was either diluted or concentrated until the number of particles in one cc. of each was some convenient whole number. When finally ready for use, No. 1 contained 40,000, No. 2 80,000, No. 3 2,000,000, and No. 4 14,000,000 particles in one cc.

5. *The Apparatus.*—The apparatus used in all the following experiments in shown in the figure. It consists of a freezing tube, *A*, with a capacity of 50 cc. To the bottom of this was soldered a tube, *B*, through which hydrogen from a generator could be admitted at any desired rate, and which served to stir the contents of the tube. The freezing tube was also provided with a two-hole stopper, *C*, carrying a thermometer, *D*, and a gas outlet tube, *E*. Surrounding the freezing tube was a liquid ammonia jacket, *F*, which served to cool the contents of the tube at an approximately constant rate. A gas regulator served to maintain the flow of the hydrogen at a nearly constant rate throughout the whole series of experiments. The rate chosen was from 350 to 390 cc. a minute, this rate being found necessary in order to avoid settling out of the coarser particles during an experiment.

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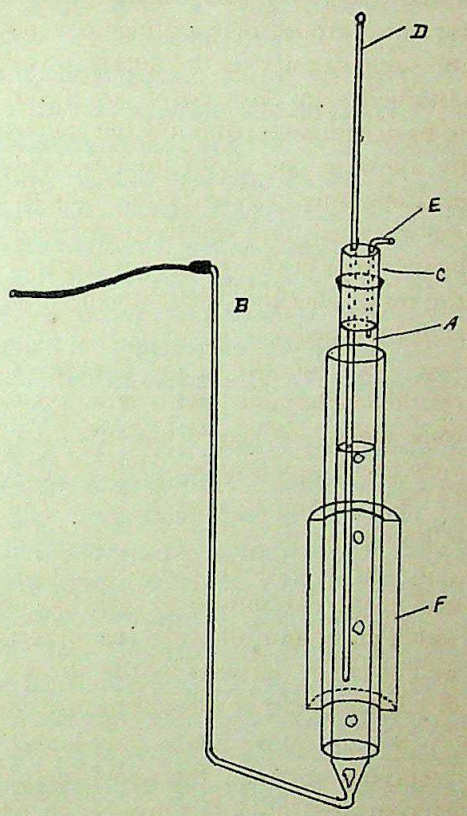
6. The Method of Experiment.—For use in these experiments a considerable quantity of redistilled water was prepared in order to have a uniform material for all the measurements. This was found advisable, as the ordinary supply of distilled water showed some variations from day to day, in its supercooling value. In carrying out a series of experiments the method was as follows:



The freezing tube was filled with the pure water to the 50 cc. mark, the flow of gas started, and several observations of the temperature at which freezing started were made. These results showed but little variation throughout the whole series of experiments, lying in general between —5.6° and —6.2°. Next a quantity of one of the above described suspensions was introduced, sufficient to produce the desired number of particles in one cc. After settling for a few moments the added water was pipetted off, the volume being again brought back to the original 50 cc.

A series of four observations (sometimes many more) was made upon the temperature at which freezing started in this suspension. Thereafter further numbers of particles were added, and corresponding observations made. In so far as it was possible, observations were made with all four sizes of particles in equal concentrations, in order to obtain results that would be directly comparable. The range in the numbers of particles per cc. was from such small values that but little effect was produced, to such large ones that the experiments could not be carried further on account of the mud-like character of the suspensions. Upon filtering these suspensions the supercooling value returned to that of the original water.

The results of these experiments are summarized in the accompanying table. The number of particles in one cc. of the suspension used is indicated at the top of each column. At the left of each horizontal column is indicated the sample of the quartz powder used. The results given are the values for Θ, that is, the amount of supercooling observed, expressed

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TABLE I.

	14,000,000.	4,480,000.	2,000,000.	500,000.	240,000.	80,000	40,000.	20,000.	15,000
No. 1.....	...	...	...	...	...	...	1.3	1.6	1.3
"	...	...	...	...	...	...	1.3	1.4	1.5
"	...	...	...	...	...	...	1.1	1.5	1.3
"	...	...	...	...	...	...	1.3	1.5	1.5
"	...	...	...	...	...	...	(1.2)	(1.5)	(1.4)
No. 2.....	...	...	...	...	...	2.0	2.7	3.2	2.6
"	...	...	...	...	...	2.2	2.1	3.3	2.7
"	...	...	...	...	...	2.1	1.8	2.6	3.2
"	...	...	...	...	...	2.2	2.0	2.9	3.5
"	...	...	...	...	...	(2.1)	(2.2)	(2.9)	(3.0)
No. 3.....	...	3.1	2.8	1.6	4.8	4.2	4.4	6.5	...
"	...	2.8	3.1	3.6	3.3	4.0	5.5	5.5	...
"	...	2.7	3.8	2.9	3.6	5.4	4.0	4.5	...
"	...	2.3	3.2	4.4	3.4	4.9	6.2	4.1	...
"	...	(2.7)	(3.2)	(3.0)	(3.8)	(4.6)	(5.0)	(5.2)	...
No. 4.....	2.7	...	3.9	3.0	4.5	3.4	6.3	...	...
"	3.3	...	4.5	4.7	5.3	6.4	6.0	...	...
"	3.2	...	3.5	3.6	5.5	6.3	3.4	...	...
"	2.8	...	4.0	5.7	5.2	5.7	5.4	...	...
"	(3.0)	...	(4.0)	(4.2)	(5.1)	(5.4)	(5.3)	...	...

	10,000.	5,000.	2,000.	1,000.	500.	100.	50.	25.	10.
No. 1.....	1.5	1.7	2.2	2.1	2.2	2.9	3.1	4.9	5.5
"	1.5	1.2	1.2	1.8	2.8	2.8	4.1	4.9	4.4
"	1.4	1.5	1.8	2.1	2.5	3.0	3.1	3.3	4.8
"	1.6	1.7	1.8	2.0	2.3	2.6	2.3	3.0	6.0
"	(1.5)	(1.5)	(1.7)	(2.0)	(2.4)	(2.8)	(3.2)	(4.0)	(5.2)
No. 2.....	3.9	4.4	4.6	3.7	5.7	4.6	...	...	...
"	4.1	3.6	4.3	5.1	5.5	5.0	...	...	...
"	3.4	4.5	4.7	5.7	5.3	5.0	...	...	...
"	3.2	4.2	4.2	5.6	3.5	5.3	...	...	...
"	(3.6)[1]	(4.2)	(4.5)	(5.0)	(5.0)	(5.0)	...	...	...
No. 3.....	5.6	...	...	...	...	...	...	...	...
"	5.2	...	...	...	...	...	...	...	...
"	3.8	...	...	...	...	...	...	...	...
"	6.8	...	...	...	...	...	...	...	...
"	(5.3)	...	...	...	...	...	...	...	...
No. 4.....	...	...	...	...	...	...	...	...	...
"	...	...	...	...	...	...	...	...	...
"	...	...	...	...	...	...	...	...	...
"	...	...	...	...	...	...	...	...	...
"	...	...	...	...	...	...	...	...	...

[1] Other series of determinations give 3.2 as the more probable average for this concentration.

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in positive centigrade degrees. The numbers enclosed in brackets are averages. In many cases far greater numbers of observations than the four given were made. In such cases the first four results obtained have been given, with one or two exceptions, to be noted later.

Discussion of the Results.

At the beginning of this paper the assumption was made that the effect of foreign particles in stimulating crystallization in supercooled liquids was a purely kinetic one, that is, that crystallization was caused by impacts between the foreign particles. From what is already known concerning the effects of impacts between larger bodies, and on the basis of the theory of probabilities, certain predictions were made as to the phenomena which should occur when definit numbers of particles of various masses were moving through a supercooled liquid at definit rates. It will now be shown that the results recorded in the above table satisfactorily confirm these predictions.

1. *The Effect of the Mass of the Particles.*—By reference to the table it will be seen that observations were made upon all the different sizes of quartz powder at a concentration (meaning number of particles) of 40,000 per cc. These results show a distinct decrease in the average amount of supercooling as the mass of the particles increases, which is entirely in accord with the prediction. Without exception, the results in the vertical columns confirm this. The fact that the results do not show a direct proportion or other simple relationship to the mass of the particles is due to several causes. Firstly, there is as yet no established quantitative relationship between impact value and crystallization stimulus. It is known that the stimulus increases with the energy of the impact, but the quantitative law which regulates these factors is not known. Secondly, the particles used were not of perfectly uniform size and were of very irregular shapes. Thirdly, the effect of the viscosity of the liquid in restricting the freedom of motion of the particles is far greater with small than with large ones. This fact may be readily predicted from the usual theory of viscosity, and ample confirmation of it will be given later.

2. *The Effect of the Number of Particles.*—By reference to the horizontal columns of the table, especially those for the two coarser samples of quartz powder (Nos. 1 and 2), it will be seen that all the predictions that were made concerning the effect of the number of particles are confirmed. At low concentrations the results are very erratic, and the average amount of supercooling is large. As the concentrations of the particles increase the average supercooling becomes less, and at the same time the results become far more uniform. When a certain concentration is reached (about 2,000 per cc. for the No. 1 powder), further increase over a considerable range (up to 20,000 for the No. 1 powder) does not further affect the results. At a concentration of 40,000 per cc. the results are

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somewhat lower. At this concentration the liquid began to show a distinct mud-like character, and it was found impossible to work at higher concentrations, since with the rate of stirring chosen, settling out of the particles could not be avoided.

With the No. 2 powder the same general phenomena are to be observed. The fact that the results do not become constant until a much higher concentration is reached is to be expected, because on account of the greater effect of viscosity in restricting the motions of the small particles through the liquid the probability of the occurrence of an impact in a given time will be less. It is however quite certain that the average of 3.6° obtained at a concentration of 10,000 per cc. with the No. 2 powder does not represent a true average. It will be observed that the first two results in this series are abnormally high. As has been stated, the results in the table are the first four obtained. As a matter of fact, ten observations were made at this point. Taking the average of these, the result is 3.2, which, if the latter result be accepted, gives a more striking confirmation of the prediction.

In experiments of this sort, where the factor of probability enters in so largely, it is of course to be expected that occasional, more or less persistent successions of abnormal results, either high or low, would be obtained, corresponding to succession of red or black in the turning of cards. In these present experiments, such successions are most likely to occur when the concentrations of the particles are small. In confirmation the following data are offered: With the No. 2 powder, at a concentration of 500 per cc., the first four results obtained give an average of 5.0 as shown in the table. Two other series of observations were made with the same sample under the same conditions. The first of these additional series contains twenty-five results, and the second six. The results are as follows:

Series 1.—6.4, 4.8, 4.4, 3.5, 3.2, 4.2, 4.8, 3.3, 3.2, 3.4, 3.2, 5.4, 5.1, 4.4, 4.0, 4.1, 4.2, 5.7, 4.0, 3.8, 3.5, 4.9, 3.2, 5.3, 5.3; average, 4.4.

Series 2.—6.3, 3.8, 4.3, 4.6, 5.1, 4.8; average, 4.8.

The average of the first four results of series 1 is 4.8, in close agreement with the result given in the table. Then begins a long and persistent series of low results, only occasionally interspersed with normal values. Series 2 was made with the same apparatus and the same sample, the only difference between the two series being that several hours had elapsed between the taking of the observations. Series 2 gives results in strict accord with the normal. Thus the large number of low results obtained in series 1 are to be looked upon as due to chance. Similar abnormalities were occasionally noted in the other series, but they were not common. With the single exception of the case above cited, the averages

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obtained from long series of readings, would, if they had been used in the table, have confirmed the predictions even more strikingly than those given. In order to avoid any possible influence from the personal equation, however, the original intention of giving only the first four results obtained was followed.

With respect to the results with the two finer powders, it will be noted that they show the same general character as those obtained with the coarser ones, except that the range in concentration throughout which the effect is independent of the concentration is less well defined. This is probably to be explained as follows; on account of the great effect of viscosity on the smaller particles, very considerable concentrations will be required before this constant range will be reached. Thus the great number of particles present may lend to the liquid a considerable mud-like character before this constant range becomes well defined.

Thus it is seen that the experiments so far described confirm in all respects the predictions made at the outset concerning the effect of the size and number of particles upon the conduct of water in regard to its supercooling. The whole effect of the foreign particles is entirely explainable upon the assumption that their activity in stimulating crystallization is due to the occurrence of impacts between them, and that this activity is a direct function of the energy value of the impacts.

Further predictions were made concerning the effect which variations in the viscosity of the liquid would produce, provided such variations could be brought about without materially affecting the other physical properties of the liquid. A few simple experiments were carried out for the purpose of determining the validity of these predictions.

3. *The Effect of Variations in the Viscosity of the Liquid.*—These experiments were carried out as follows: First, the supercooling value was determined for a sample carrying a known number of quartz particles of a known size; a small known quantity of gelatin solution of known concentration was then added, which served to materially increase the viscosity of the liquid; finally its supercooling value was determined. The following table summarizes the results of a number of experiments of this character. In column 1 is indicated the sample of quartz powder used. In column 2 is given the number of particles of quartz per cc. Column 3 gives the concentration of the gelatin in the liquid. Column 4 contains the supercooling values for the water with the indicated number of quartz particles, but without the gelatin. In column 5 are given the supercooling values for the samples after the addition of the gelatin. All the supercooling values given are averages of a considerable number of determinations:

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TABLE II.

Powder used.	Particles per cc.	Conc. of gelatin per cc.	Supercooling values. Without gel.	With gel.
No. 1	1,500	0.10	1.8	2.4
No. 2	100	0.20	4.8	6.1
No. 3	40,000	0.05	4.5	5.6
No. 4	280,000	0.05	4.4	6.9
None	...	0.05	5.7	7.2

These results show very clearly the protective influence of the gelatin. The protection increases as the particles used decrease in size, in spite of the fact that the smaller particles are used in far greater concentrations, while at the same time the concentration of the gelatin is less. The protection in the case of the No. 2 powder is slightly greater than that within the No. 3, which is, however, to be ascribed to the fact that four times the concentration of gelatin was used.

The results obtained with water to which no particles were added show a smaller specific protection than that found for the No. 4 quartz powder. This is partly due to the fact that the distilled water is comparatively free from particles, whence less protection is possible, and partly to the fact that at such low temperatures the sensitiveness of the water to crystallization stimulus is very great. Thus a specific protection of one degree at these low temperatures is of much greater significance than the same protection at higher ones. It is to be noted that the protected value for water without particles is the lowest obtained.

Thus the predictions made at the outset seem to be confirmed without exception. These predictions were made upon the assumption that the crystallization stimulus is a purely kinetic phenomenon, and this assumption seems to be reasonably justified by the results of the preceding investigation. It is not, however, to be concluded that impact is the only form of mechanical stimulus possible. For example, it might be the case that a particle in rapid rotary motion would serve as a more effective stimulus in some cases than an impact of the same energy value. At the present time there is no evidence from which conclusions upon this point may be drawn. It is also possible that stimuli not mechanical in character may be discovered, although none seem to be known at present. Several attempts to induce crystallization under the influence of electrons have been made in this laboratory, but without success.

It may be not without interest to attempt to apply the above principle to the explanation of the conduct of supercooled liquids at rest with respect to their spontaneous crystallization. As is generally known such conduct is highly erratic. Under apparently identical conditions, identically prepared samples give the most diverse results. Of a number of samples some may crystallize in a few minutes, and others only after hours or even weeks. In the light of the foregoing investigation, such

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results seem readily explainable. Most such investigations have been carried out with liquids not freed from foreign particles, and the fortuitous manner of their crystallization is readily explained. It has been repeatedly observed that the effect of long continued heating of a liquid is to increase its average supercooling value. This is explainable as due in the main to the disintegration and perhaps solution of some of the particles existing in the liquid.

Jaffé[1] has shown that the supercooling value may be much increased by filtration, which is, of course, to be looked upon as due to the removal of small particles. He has also noticed that in a liquid which remained at rest for a considerable time, crystallization was most likely to start from the bottom of the tube. This is, of course, due to the slow accumulation of particles at the bottom of the tube by settling.

It has been frequently observed that greater supercooling is possible in a small body of liquid than in a large one. Two factors probably contribute to produce this result: First, in a small body less convection currents, and consequently less agitation among suspended particles will occur; secondly, under otherwise like conditions the probability of the occurrence of an impact will be less in a small volume than in a large one, especially in the case of liquids in which particles are very sparsely distributed; this latter factor may be of great importance.

Tammann[2] has shown that the number of crystallin nuclei which appear in a supercooled liquid increases with the supercooling, reaches a maximum value at a temperature corresponding approximately to the temperature of the maximum crystallization velocity, and thereafter falls off. A little thought will show that the same factors which cause the maximum in the crystallization rate should also cause a maximum in the number of crystals which can start within the liquid. Assume a liquid charged with a considerable number of particles. As this becomes more and more supercooled, its sensitiveness to mechanical crystallization stimulus increases, and the number of effective impacts in a given time will increase. When the viscosity increases materially, it will tend to restrain the motions of the particles, and the probable number of effective impacts in a given time will decrease.

One other point only remains to be considered. The query naturally occurs as to what would be the conduct of a particle-free liquid at rest, and cooled in such a way that convection currents and other mechanical disturbances are avoided. Would crystallization ever occur in such a system? The answer must be that it is perfectly possible that such crystallization might occur. The mere instantaneous appearance within the liquid of a molecule possessed of a kinetic energy considerably above

[1] *Z. physik. Chem.*, 43, 565.
[2] *Ibid.*, 25, 441.

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the average might produce sufficient disturbance to start crystallization when the liquid had reached an extremely sensitive condition. If, however, before reaching so sensitive a state, the viscosity of the liquid had reached a great value, the likelihood of such an occurrence would be correspondingly small. Tammann's investigations[1] showed that many liquids could be cooled to amorphous solids without great difficulty. The method is merely that of cooling very quickly, and its effectiveness depends upon the avoidance of the necessary mechanical stimuli to crystallization by not allowing them time to occur.

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RADIOACTIVITY.[2]

BY ANDRE DEBIERNE.[3]

Received July 1, 1911.

Radioactivity comprises to-day a very large number of facts and theories of which it would not be possible to give a complete survey in a brief address. Nevertheless, I shall make an effort to bring out all the chief points of interest of the new science, the birth of which may be considered without exaggeration as the most important scientific event of the past few years.

Not only has this new science revealed the existence of extremely curious substances and brought a rich harvest of new natural phenomena, but it has led us to the attack of a problem which seemed absolutely chimerical only a few years ago—the problem of the transmutation of atoms or of the chemical elements; for it is now demonstrated that the phenomena of radioactivity are concomitants of the disintegration of atoms. Radioactivity may now be defined as the science of atomic transformations; it is not impossible that in time radioactivity may become the art of changing chemical elements into one another. The facts known at present leave no doubt as to the reality of atomic disintegrations; if as yet these transformations are entirely beyond our control, possibly some day we may learn how to bring them about and to control them.

The fundamental phenomenon, which was discovered by Henri Becquerel and has served as the point of departure for the development of radioactivity, is as follows: Certain substances emit spontaneously a peculiar radiation whose properties are analogous to those of the rays obtained in a Crookes tube. The new rays render gases conductors of electricity, act on a photographic plate, and produce fluorescence in certain substances. This spontaneous emission of rays was first observed in the case of uranium and its compounds, later also in the case of thorium compounds. Then were discovered new substances possessing the same property in a very high degree. All these substances are said to be *radioactive*. They constitute a new source of energy.

An apparently essential characteristic of the phenomenon of radio-

[1] *Loc. cit.*

[2] A summary presented at the Second Decennial Celebration of Clark University, Worcester, Mass., September 17, 1909.

[3] Translated from the French by M. A. Rosanoff.

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activity is its spontaneity: the emission of rays takes place without visible external cause. This characteristic permits of distinguishing the phenomena of radioactivity from those that take place in the course of certain chemical reactions. For instance, the oxidation of phosphorus is accompanied by phosphorescence and by electrical conductivity of the gases surrounding the phosphorus. The same phenomena may be brought about by the action of heat upon the sulfate of quinine. But in all such cases the phenomenon is not spontaneous; it is brought about by external causes which are easy to detect. Therefore, phosphorus and quinine sulfate are not considered as radioactive substances.

Another essential characteristic was brought out by the early researches of Madame Curie. Radioactivity is an atomic property. The spontaneous emission of rays is connected with the radioactive *atom*, and is not in the slightest degree influenced either by changes of state of aggregation of by chemical combination with the atoms of other elements. Thus, the intensity of the Becquerel rays emitted by the substances containing uranium, and measured by the conductivity of the surrounding gases, is always proportional to the number of uranium atoms contained in the substance and is independent of the form in which uranium may be present. Among the numerous other properties of matter, mass alone is so distinctly atomic in its nature.

Our realization of the atomic character of the radioactive property has had a directing influence on the science of radioactivity and has led to the establishment of its present theories. But first of all it had led to the discovery of radium itself and of the other strongly radioactive substances. I shall review briefly the genesis of the discovery of radium, which forms one of the most beautiful investigations ever carried out in the physical sciences, both as regards the logical keenness with which the research was carried on and as regards the material difficulties which had to be overcome. The novel method employed has since been constantly used in researches in radioactivity.

Among the elements that had previously been known, only uranium and thorium were radioactive, and the activity of any substance containing one of these elements was found to be proportional to the quantity of the active element present. Certain minerals, however, containing uranium showed a greater activity than metallic uranium itself. Pierre Curie and Madame Curie, thoroughly convinced of the atomic nature of radioactivity, assumed that these minerals contained new chemical elements, endowed with greater activity than uranium, and although physicists by profession, and with only rudimentary laboratory means at their disposal, they undertook a search after the new hypothetical elements.

I cannot depict here all the difficulties that presented themselves in the search, which involved the chemical treatment of tons of material. Suffice it to recall the results obtained by Pierre Curie and Madame Curie after several years of uninterrupted effort. Those results fulfilled their expectations entirely. The minerals studied do contain strongly radioactive compounds, whose radioactivity is due to the presence of new chemical elements. In the case of one of these elements, namely, radium, it has been possible to prepare a series of pure salts; further, its spectrum has been studied, its atomic weight determined and a place has been

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assigned to it in the periodic classification of the elements. Radium has become a marvelous instrument of research, and to it we owe all the most important discoveries in radioactivity.

It was soon recognized that radioactive substances may differ from one another, not only in intensity of radiation, but also in the character of radiation and in certain peculiarities in the mode of emission of the rays. On the basis of these properties it is as easy to recognize a given radioactive element with certainty as it is to recognize one of the older elements with the aid of spectrum analysis.

The principal new radioactive substances are polonium and radium, discovered by Pierre Curie and Madame Curie; actinium, discovered by myself shortly afterwards; radio-thorium, discovered by Hahn; and ionium, discovered by Rutherford and Boltwood. However, certain of these substances are really complex mixtures containing entire families of chemical elements: namely, the thorium family, the radium family, and the actinium family.

The rays emitted by radioactive substances may be subdivided into three groups, *viz.*, the α rays, the β rays, and the γ rays, which are analogous to the three groups of rays emitted in a Crookes tube, *viz.*, canal rays, cathode rays, and Roentgen rays. The α rays are constituted by the projection of positively charged particles; the β rays by a projection of negatively charged particles; the γ rays are not charged at all.

The particles of β rays are *electrons*, and the rays are easily bent out of their path by a magnetic field. Certain β rays are constituted by electrons projected with an extremely great velocity, a velocity approaching that of light, and it has been possible to verify on these rays an important deduction from the electron theory. For very great velocities, namely, the inertia of a particle ceases to be a fixed quantity; it may greatly increase with increased velocity of motion, and so the particle no longer obeys the laws of Newtonian mechanics. Finally, comparing β rays and cathode rays, one finds them analogous, only the particles of β rays move with greater velocity and are capable of penetrating a much thicker layer of matter (for instance, a plate of aluminium one mm. thick).

The α rays are constituted by the projection of *material particles*, charged electro-positively, having the dimensions of atoms, and moving with a smaller velocity than the particles of β rays. The α rays are bent by a magnetic field with considerable difficulty, and can penetrate only a very thin layer of matter (aluminium foil $^1/_{20}$ mm. thick absorbs them completely). They have the peculiarity of suddenly stopping after having traversed a certain well-determined path in a given medium. The length of this path in air is a very important quantity, for it permits of distinguishing from one another the different species of α rays and consequently also the different radioactive substances. The α particles play a very important part in radioactive transformations, and their nature seems now to be clearly understood.

The γ rays are not charged, and therefore are not deflected by a magnetic field. They suffer but slight absorption in matter (a considerable proportion of the γ rays from radium passes through a lead plate one centimeter in thickness).

These several rays excite fluorescence in a number of substances (platino-

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cyanide of barium, sulfide of zinc, uranyl salts, glass, paper, diamond, etc.). The action of α rays upon zinc sulfide produces the very peculiar phenomenon generally designated by the term *scintillation*; in this, the luminosity of the zinc sulfide screen is caused by an infinity of brilliant little points which appear and disappear continually and which are clearly distinguishable when the screen is examined with a lens.

The radioactive substances constitute a new source of energy; but during the earlier researches both the origin and the mechanism of this production were entirely unknown. Pierre Curie and Madame Curie advanced two distinct hypotheses to explain the production of this energy. The first hypothesis assumed that the energy was furnished from outside in the form of a special radiation, causing in the radioactive substances a phenomenon analogous to phosphorescence. According to the second hypothesis, the energy comes from the active substance itself, and hence the emission of energy must be accompanied by a change in the substance. Pierre Curie and Madame Curie, who had demonstrated the atomic character of the new property, believed thoroughly, even before radium had been discovered, that the transformation takes place in the radioactive atom itself, which must therefore change into a different atom and, consequently, gradually disappear in course of time. It is this hypothesis of atomic transmutation that has proved to be most fruitful and has formed the basis of the theories accepted at present.

The principal fact which has led to these theories is as follows: With the aid of radioactive substances, whose activity appears constant and permanent, it is possible to produce phenomena of radioactivity whose intensity diminishes in time. These phenomena of temporary activity may be observed under various circumstances. Thus, if any substance whatever is placed near a salt of radium, thorium, or actinium, the surface of the substance becomes radioactive, and this activity diminishes more or less rapidly in time. This is the phenomenon of induced radioactivity discovered by Pierre Curie and Madame Curie. Similarly, any gaseous atmosphere surrounding radium, thorium, or actinium, becomes itself radioactive, and its activity likewise diminishes in time. Rutherford, the discoverer of this last phenomenon, gave the name "emanation" to the cause of the temporary activity of the gases. Finally, as first observed by myself, in the case of actinium, substances temporarily radioactive may also be obtained through certain chemical separations in mixtures containing permanently radioactive substances.

These temporary radioactivities often follow complex laws of decrease. The study of these laws has shown that there exist really several different kinds of radioactivity succeeding one another in time. When one kind of activity has died out, another replaces it, and this may gradually cease to exist in its turn. Each kind of radioactivity is characterized by its own velocity of decrease and by a radiation peculiar to itself. Extraordinarily great temporary radioactivities may accumulate in an extremely slight quantity of matter.

Applying to these temporary radioactivities the idea which had guided to the discovery of radium, namely, that radioactivity is an atomic property of the elements exhibiting it, one is led to think that the temporary radioactivities which have been separated from radium, thorium, and actinium characterize new radioactive atoms. And, accepting the

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hypothesis of atomic transmutation as an explanation of the origin of radioactive energy, the decrease of a given radioactivity appears to result from the gradual disappearance of a radioactive element and its transmutation into another element.

The present theory of radioactive phenomena is based on these considerations. It was proposed by Rutherford and Soddy, who have published numerous observations in complete accord with it. At present the theory is accepted by all investigators of radioactivity. An extremely precious guide in research, it has again and again been confirmed by discoveries of great importance.

The various phenomena exhibited by radium may, then, be interpreted as follows: The radium atom, which emits a certain α radiation, produces continually a radioactive emanation. This emanation is considered to be a radioactive gaseous element resulting from the transmutation of radium, and hence the latter must gradually disappear in time. The emanation emits an α radiation different from that of radium and disappears quite rapidly (the decrease follows a simple exponential law and amounts to one-half in 3.8 days). The emanation produces deposits of induced radioactivity, which are considered as new elements resulting from the transmutation of the emanation. In these deposits it has been possible to identify a series of stages which have received the names of Radium A, Radium B, Radium C, and which succeed one another, radium A changing into radium B, which in turn changes into radium C. These different members of the group emit different radiations and undergo destruction with considerable velocities.

Following radium C is another sequence of terms, characterized by a much smaller rate of disappearance, *viz.*, Radium D, Radium E_1, Radium E_2, and Radium F. The last-named has been shown by Rutherford to be identical with polonium. Polonium itself disappears little by little, but the element succeeding it is as yet unknown.

It has been possible to determin with much precision the laws of formation and destruction of the different transition terms of the series. These laws are exponential expressions analogous to those which hold for monomolecular chemical reactions. Most of the terms have been isolated (by means of chemical reactions, electrolysis, heating, condensation at low temperatures, etc.), and the several exponential formulas followed by their rates of destruction have been determined separately, the formula corresponding to each term having a characteristic exponent, λ, of its own. The rate of destruction of a given term is frequently characterized by specifying the time T required to diminish by one-half the original intensity of its radiation. The quantity $1/\lambda$ may be considered as the mean duration of life of an atom of the substance under consideration; it is denoted by the symbol Θ and is usually referred to briefly as "the mean life." We have, then, $\Theta = 1/\lambda$ and $T = \Theta \ln 2$.

The numerous researches which have been carried out on radioactive substances have resulted in fairly complete knowledge concerning the series of radioactive transformations in the several families, the properties of the different terms, and the properties of the rays emitted during the transformations. The knowledge gathered up to the present time is reproduced in the accompanying tables.

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Active substance.	Destruction period T.	Radiation.	Path of α rays.	Absorption coefficient of β rays.	Absorption coefficient of γ rays.	Various properties.
Uranium	6×10^9 years (order of magnitude)	α	3.5 cm.			At. wt. 238.5. Well known chemical properties.
↓ Radio-uranium						Partly carried down by barium sulfate.
↓ Uranium X	20.7 days	β,γ		2 groups: $\mu_1 = 14.4$ $\mu_2 = 510$	$\mu = 7.4$	Prepared from uranium with iron hydroxide and bone-black, more soluble in water than in ether.
↓ ? ↓ Ionium	1500 years (?)	α	2.8 cm.			Properties identical with those of thorium.
↓ ? ↓ Radium	2000 years	α	3.5 cm			At. wt. 226.5. Group of alkaline earths. Luminous salts. Evolves heat (1 gram of radium in radioactive equilibrium evolves 118 calories per hour; 20 per cent. of this is produced by radium itself). The principal rays of the characteristic spectrum of radium are 4340.6; 3814.7; 3649.6. One gram of radium in equilibrium evolves 0.37 cubic millimeters of helium per day. The ionization produced by 1 gram of Ra in equilibrium equals that produced by 7,300,000 grams of uranium.
↓						

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Active substance.	Destruction, period T.	Radiation.	Path of α rays.	Absorption coefficient of β rays.	Absorption coefficient of γ rays.	Various properties.
Radium emanation	3.86 days	α	4.23 cm.			Inert gas. Principal lines of the characteristic spectrum: 4349.8; 4166.6; 3981.6. The emanation in equilibrium with 1 gram of Ra occupies 0.60 cubic millimeter under a pressure of 1 atmosphere.
↓ Radium A	3.0 minutes	α	4.83 cm.			The deposit of induced activity is volatil at 800–900°. Soluble in strong acids.
↓ Radium B	26.7 minutes	β		from 13 to 890		The deposit of induced activity is volatil at 600–700°. Precipitates together with $BaSO_4$.
↓ Radium C	19.5 minutes			13 to 53		The deposit of induced activity is volatil at 1000–1300°. Is deposited on nickel and copper in acid solution. Radium B and radium C can be separated by electrolysis.
↓ Radium D	12 years (?)	No rays				Properties identical with those of lead. Volatil below 1000°.
↓ Radium E_1	6.3 days	No rays				Can be separated from radium D by boneblack and also by electrolysis.
↓ Radium E_2	4.8 days	β		40		
↓ Radium F or polonium	140 days	α	3.86 cm.			Is deposited on Bi, Cu, Sb, Ag, and even Pb. Sulfide insoluble. Carried down with basic salts of bismuth. Precipitated by $SnCl_2$. Volatil toward 1000°.

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↓ ? (unknown term)						The substance known as radio-lead is a mixture of radiums D, E_1, E_2, F.
Thorium	3×10^{10} years	α	3.5 cm.			At. wt. 232.4. Known chemical properties.
↓ Mesothorium I	5.5 years					
↓ Mesothorium II	6.2 hours	β,γ		20 to 39	0.5	
↓ Radiothorium	2.0 years	α	3.9 cm.			
↓ Thorium X	6.64 days	α	5.7 cm.			Partly soluble in ammoniacal solutions.
↓ Thorium emanation	53 seconds	α	5.5 cm.			Inert gas. Condenses toward —120°.
↓ Thorium A	10.6 hours	β		140		The deposit of induced activity is soluble in strong acids.
↓ Thorium B	55 minutes	α	5.0 cm.			Deposit of induced activity. Is deposited upon nickel from acid solution. Carried down by boneblack. May be separated from thorium A by distillation or by electrolysis.
↓ Thorium C	very short	α,β,γ	8.6 cm.	15.7	0.5	
↓ Thorium D	3.7 minutes.	β		very penetrating		
↓ ? (unknown term)						

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Active substance.	Destruction, period T.	Radiation.	Path of α rays.	Absorption coefficient of β rays.	Absorption coefficient of γ rays.	Various properties.
Actinium	very long	No rays				Group of rare earths.
↓						
Radioactinium	19.5 days	α	4.8 cm.			May be separated by electrolysis or by fractionation with ammonia.
↓						
Actinium X	10.5 days	α,β	6.55 cm.	170		Soluble in ammoniacal solutions; can be separated by electrolysis.
↓						
Actinium emanation	3.9 seconds	α	5.8 cm.			Inert gas. Condenses between —120° and —150°.
↓						
Actinium A	36.1 minutes	β		highly absorbable		Deposit of induced activity. Soluble in strong acids. Volatil at 400°.
↓						
Actinium B	2.1 minutes	α	5.5 cm.			Can be separated from the preceding by electrolysis. Volatil at 700°.
↓						
Actinium C	5.1 minutes	β,γ		29	2.0 to 3.6	Carried down by boneblack or by platinum sponge.
↓						
? (unknown term)						

Remark I.—The absorption coefficients of the β and γ rays refer to aluminium and are expressed in cm.$^{-1}$ units.

Remark II.—Potassium salts possess a slight radioactivity, which seems to come, not from radioactive impurities, but from the potassium atom itself; β rays are emitted.

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The inter-relation between the different terms of one and the same family is not the result of theoretical interpretation. It is a thoroughly established experimental fact. According to present-day theory, each term represents a certain chemical element which differs from the ordinary elements only by its ephemeral existence and by its emitting a special radiation. The disappearance of the radioactive atom is the result of its transformation into another atom, the special radiation representing the energy which accompanies that transformation. According to this theory, then, the study of radioactivity has led to the discovery of some thirty new elements.

The theory outlined above permits of an easy interpretation of all phenomena thus far known. Still, it was a matter of great importance to obtain a direct experimental demonstration of the reality of atomic transformations, and of the existence of chemical atoms having a very short life, corresponding to the ephemeral radioactivities. Such direct experimental demonstrations have actually been produced, and hence the theory rests on an extremely solid basis.

The reality of atomic transformations accompanying the phenomena of radioactivity has been demonstrated by the experiments of Ramsay and Soddy on the production of helium from radium. Radium, whose character as a chemical element is established by its chemical properties, by its atomic weight, and by its spectrum, continually produces the gas helium, which is itself a well characterized chemical element. This production of helium cannot be reasonably interpreted in any other way than by recognizing atomic transformation.

Some time after Ramsay and Soddy, I showed that the same phenomenon takes place in actinium, which also continually produces helium gas. Recently, Soddy has discovered the production of helium also from uranium and from thorium.

The production of helium from radioactive substances is the first case ever discovered of the transformation of chemical atoms.

That an ephemeral radioactivity is due to the existence of a corresponding chemical element has been experimentally demonstrated in the case of the radium emanation. This emanation has been isolated in a pure state, its spectrum determined, and its volume measured. Somewhat numerous experiments were first carried out by Ramsay and his collaborators, and though the published results are not in perfect agreement, they still leave no doubt whatever as to the material existence of the emanation, which is characterized by a spectrum of its own. The isolation of the substance was effected by utilizing its property of easily condensing at low temperatures. These experiments were later repeated by Rutherford and Royds, who obtained agreeing measurements of the volume occupied by the pure emanation produced by a given quantity of radium, and who described completely the spectrum of the emanation. Recently, I have carried out analogous experiments: my volume measurements agree perfectly with Rutherford's, and my spectrophotographs are identical with those of Rutherford and Royds. I have observed besides that the volume of gas produced does not increase proportionally to the time, owing to the spontaneous destruction of the substance. The observed volume is invariably proportional to the radioactivity of the emanation, no matter what the duration of its production from radium. In the experiments mentioned above, all investiga-

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tors have observed the production of helium from the emanation: the spectrum of helium gradually appears, while that of the emanation disappears. Finally, Rutherford, and also Ramsay, have succeeded in determining the point of liquefaction and the point of solidification of the emanation.

It thus appears entirely certain that the emanation is a material gas—a fact which corroborates very strongly Rutherford and Soddy's theory.

The production of helium by radioactive substances is directly related to the emission of α particles, and the hypothesis early advanced by Rutherford, that each α particle is an atom of helium, is to-day confirmed. In fact, Rutherford has shown that the α rays and the helium produced by the radium emanation pass through thin layers of matter in a similar manner. Other properties of the α particles are in complete accord with this conception of their nature.

Now, if we assume that in all transformations accompanied by the emission of α particles each radioactive atom changes into the next in order by loss of a single α particle or helium atom, it becomes possible to calculate the atomic weights of the several transition elements of the radium series. The atomic weight of helium being 4, we have, namely: Radium 226.5 $\longrightarrow$ Emanation 222.5 $\longrightarrow$ Radium A 218.5 $\longrightarrow$ Radium B 214.5 $\longrightarrow$ Radium C 214.5 $\longrightarrow$ Radium D 210.5 $\longrightarrow$ Radium E 210.5 $\longrightarrow$ Radium F, or Polonium, 210.5 $\longrightarrow$ a last unknown substance 206.5. This last number represents exactly the atomic weight of lead, which suggests the idea that this element is the final product of the transformation of radium. It is probable that this idea can be subjected to experimental verification.

The mother substances, uranium, radium, actinium, and thorium, ought to gradually disappear in course of time, as they are transformed into other elements. But the destruction is certainly very slow, and no diminution of their activity has been directly detected. The laws of their destruction may, however, be determined indirectly. Since the transformation of each radioactive atom produces an emission of rays, it is natural to assume that the more intense the radiation produced by a gram-atom of the substance, the more rapid is the transformation. Thus, radium ought to have a much shorter life than uranium or thorium. The comparison of the radiations may be carried out quantitatively, and thus the ratio of the mean lives of two radioactive substances may be readily obtained.

On the other hand, if it is assumed that the emission of a single α particle corresponds to the transformation of a single atom, it will suffice to determin the number of particles emitted per second by a given mass of the active substance under consideration, in order to ascertain its velocity of transformation. Indirect determinations were first made by measuring the total positive charge emitted in the form of α rays by the active substance and making an assumptiion concerning the charge of a single particle. The results so obtained have been confirmed by directly counting the α particles emitted by a certain quantity of active substance.

The first direct results were yielded by the scintillations produced by α particles on a screen of zinc sulfide. Each scintillation being assumed to be produced by a single α particle, the number of scintillations was

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determined, produced in a given time by a known quantity of the active substance. This gave the number of α particles emitted by the substance, and consequently the number of atoms transformed in a given time. Another, and very ingenious, method was first employed by Rutherford and Geiger, who utilized the ionization produced in a gas by α particles. These investigators succeeded in determining the ionizing effect produced in a rarefied gas by each α particle by making use of the phenomenon of ionization by shock. The entrance of each single α particle into the gas affects the electrometer, and all that is necessary is to count the number of disturbances produced in a given time. The two methods have yielded well agreeing results, which indicate that radium ought to be one-half destroyed in about 2000 years.

The destruction of radium is too slow to be capable of being detected by direct experiment. Nevertheless, in order to account for the presence of radium in minerals, it is necessary to assume that radium is continually produced in those minerals, the destruction being thus partly compensated for. The element which appears evidently to be the most capable of changing into radium is uranium.

In fact, radium is always found in uranium minerals and, furthermore, uranium is radioactive and hence in a state of decomposition. Since the radioactivity of uranium is much less intense than that of radium, its duration of life must be much greater than that of radium, and this explains the occurrence of uranium in considerable quantities in nature.

An extremely important argument in support of the accepted relationship between uranium and radium lies in the constant ratio of the quantities of the two elements found in minerals. The constancy of this ratio, which has been principally affirmed by the experiments of Boltwood, is readily explained if we assume that radium is produced from uranium, and that the destruction of radium is much more rapid than that of uranium. The ratio permits of calculating the mean life of uranium.

Attempts to demonstrate directly the formation of radium from uranium have shown that this transformation is certainly not immediate, and that there ought to exist at least one substance intermediate between uranium and radium. This has been confirmed by Rutherford and Boltwood's discovery of a new substance capable of producing radium. This new substance has been named ionium. The mean life of ionium being probably long, there is hope that this substance will be isolated without much difficulty.

The question of the relationship between uranium and radium seemed to be definitly settled, when recently Mlle. Gleditsch announced that the ratio of the quantities of uranium and radium was *not* the same in all minerals, contradicting the earlier results of Boltwood. While the ratios found by Mlle. Gleditsch are of the same order of magnitude, they nevertheless differ very materially from one another. The hypothesis of the formation of radium from uranium furnishes so simple an explanation of the presence of radium in minerals that one can hardly abandon it. As a matter of fact, however, the conditions of formation of radium appear to be complex and not yet completely elucidated. Unquestionably, further study of the relative quantities of the different active substances in minerals will yield new and important results. Such study will also be of great usefulness in geology.

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If the phenomena of radioactivity indicate atomic transformation, one expects to find radioactive energy, corresponding to the transformation of atoms, to be far greater than the energy changes generally accompanying the transformation of molecules. That this is true is shown by Pierre Curie and Laborde's discovery of the enormous quantity of energy given off by radium. One gram of radium in radioactive equilibrium would produce about 120 calories of heat in an hour. The quantity of heat that would be set free by the complete transformation of one gram of radium is nearly the same as that produced by the combustion of a ton of coal. Most of this heat has been shown to come from the kinetic energy of the α particles. Heat has also been shown to be developed by actinium, thorium, and polonium. Radioactivity thus constitutes an extremely important source of energy. A very slight proportion of radium in the sun (about 1 gram per cubic meter) would be sufficient to account for all the energy radiated by it. The energy radiated by our own planet seems to be more than compensated for by the radium contained in its crust, so that the progressive cooling of the earth, once generally accepted, now seems to be problematic. It seems legitimate to assume that radioactivity constitutes one of the principal sources of the energy radiated in the universe. No other hypothesis is based on an equally serious experimental foundation.

The atomic transformation of radioactivity takes place under very peculiar conditions. As already stated, the phenomenon is spontaneous, apparently causeless. Moreover, no method is as yet known by which such transformations might be brought about or stopped, or even in the least degree hastened or slowed up. Elevation of temperature, which is so sure to increase the velocity of chemical reactions, seems to have no effect whatever on radioactive transformations. Thus, the characteristic constant of the destruction of radium emanation is the same at high temperatures as at the temperature of liquid air. Neither does the nature of an inactive chemical element combined with the radioactive atom seem to have any influence upon the velocity of its destruction. As yet, we are mere spectators, observing the transformation of atoms, but unable to interfere with it in any way.

The transformation follows a probability law identical with the law of mass action followed by chemical reactions: the number of atoms transformed per unit of time is at any instant proportional to the total number of atoms present. No simple and satisfactory hypothesis, however, has been advanced explaining this fact. In the case of mono-molecular chemical reactions, the fact that the transformation takes place gradually is explained on the assumption that all the molecules present are not in the same condition, either owing to collisions between the molecules or because of differences in whatever motion may be going on within the molecules themselves. The transformation of a given molecule is instantaneous, but the molecule will not undergo transformation unless it happens to get into a certain condition necessary for it. The probability law must then remain the same as long as the number of molecules remains very great and the external conditions of the reaction remain the same. In the case of radioactive transformations, external conditions (*e. g.*, of temperature) and intermolecular collisions ought to have no effect. Therefore, only the motion within the interior of the atom

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can be invoked in an effort to explain why, in one and the same substance, some atoms break down immediately after being formed, while others are destined to live hundreds or even thousands of years before undergoing transformation.

It is imaginable that there exists in space a special field of force which influences intra-atomic motion and is therefore capable of causing the disintegration of atoms. The action of such a force must then be independent of any translatory motion of the atoms. There is, however, at present absolutely no indication of the existence of such a force in space.

If the transformation is *not* brought about by an external force, and if external conditions of pressure, temperature, etc., have really no influence upon the progress of radioactive changes, one is led to assume that the destiny of a given atom is completely determined at the very moment of its formation, that at that moment it is already in such a state that its transformation must take place after exactly a certain interval of time. In that case a radioactive element must be considered as made up of atoms of different nature, some destined to very speedy destruction, others to a more or less prolonged existence. It is not unthinkable that these different atoms of one and the same radioactive element may some day be separated.

In order to account for the exponential law of spontaneous destruction, it is necessary, in that case, to assume that the distribution of life durations among the atoms at the moment of their formation is represented by a simple exponential function, the atoms of short life being much more numerous than those of long life. It is, however, difficult to imagine what can possibly be the cause of such a law of distribution, and considerations like the above only show that while the laws of radioactive transformations have been determined with precision and are well known, the initial cause of the phenomena is as yet altogether obscure.

In concluding this summary, I will mention the attempts that have been made with a view to artificially bringing about atomic transformations with the aid of radioactive energy. Some results in this connection have been published by Ramsay and Cameron. They believed that by the action of radium emanation upon water they had succeeded in producing neon. They further believed that by the action of the emanation upon a salt of copper they had produced alkali metals: the formation of lithium appeared to have been especially well demonstrated.

These results have, unfortunately, been shown to be erroneous. Mme. Curie and Mlle. Gleditsch repeated the experiments on the formation of lithium and found that when no other than platinum vessels were used, the appearance of lithium could not be detected; in Ramsay and Cameron's experiments the lithium came from the glass of the apparatus employed. Similarly, Rutherford and Royds have re-investigated the effect of emanation upon water and have failed to obtain any neon. I, too, have failed to find neon in the gases evolved by a solution of radium. The neon found by Ramsay and Cameron must have come from a small quantity of air introduced by accident.

So it may be said that up to the present time no atomic transmutation has been produced artificially. All we can do is to subject to inquiry spontaneous transmutations which we cannot control. A long step,

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therefore, remains to be taken before the dream of the alchemists has been realized.[1]

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NOTES.

An Electrically Heated Sealed Tube Furnace.—A sealed tube furnace must, frequently, be allowed to run over night and, at the same time, admit of being easily moved from place to place. The danger from fire, involved when heated by the ordinary burner, as well as the impossibility of keeping a uniform temperature without a temperature regulator, in many cases, makes the use of electricity very convenient as a means of heating.

This is very readily accomplished by means of nichrome resistance wire covered with asbestos (this wire can be obtained from the Driver-Harris Wire Co., of Harrison, N. J.). With this wire it is possible to make the windings directly on the iron tubes of the furnace without danger of short circuit at the temperature customarily used in these furnaces.

The furnace in question was made by covering each of the two tubes, in an ordinary sealed tube furnace, with one layer of thin absestos paper (an advisable precaution) and then winding with 55 feet of No. 22 B. S. asbestos covered, nichrome resistance wire. The wire was wound somewhat closer at each end than in the center of the tube, this making an even distribution of heat throughout the length of the tube. Under these conditions about 2 amperes were used when connected in parallel to a 110 volt circuit and 1 ampere when connected in series. This gave temperatures of 150° and 250° within the tubes. When the space within the box around the iron tubes was filled with asbestos fiber and magnesium oxide, temperatures of 240° and 440° were obtained. If checked occasionally a resistance box marked with the temperatures corresponding to the different steps will give a very satisfactory means of regulating the temperature.

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A Handy Buret-Holder.—Being obliged, on an occasion three years ago, to work with a small traveling laboratory forty miles from the base of supplies, it became necessary to improvize a compact support for a

[1] New results have been published by Ramsay and Gray. According to these investigators, carbon dioxide may be produced by the action of radium emanation upon compounds of thorium, zirconium, silicon, etc. But inasmuch as carbon compounds may easily find their way into apparatus by accident, it is difficult to establish beyond doubt a transformation of the elements thorium or zirconium into carbon. The authors themselves admit that their experiments are not conclusive.

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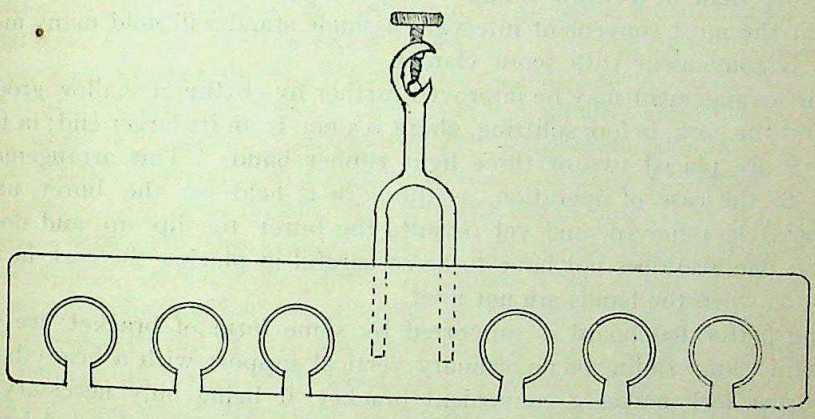
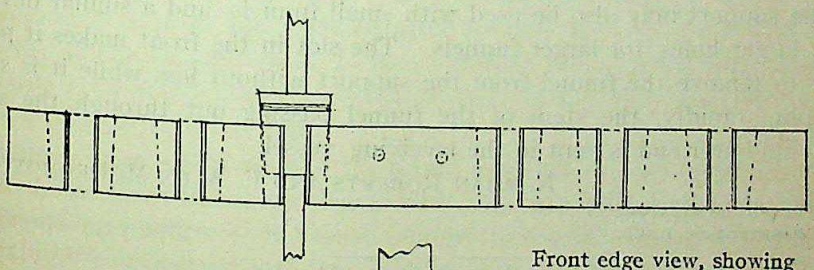
considerable number of burets. The resulting device was more satisfactory than the conventional article, and we now use it constantly.

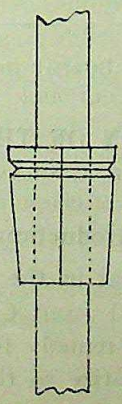
A piece of board of suitable size (*e. g.*, 50 × 8 × 2.2 cm.) is bored, a little in front of the middle, with a row of holes about 2.5 cm. in diameter and 5 cm. between centers. These holes are then connected with the front of the board by saw-cut slots about 1.7 cm. wide. All edges are rounded and sandpapered, the bored holes being filed out so as to be slightly conical with the base up. Conical corks are then selected to fit the holes so that



Top view, with burner-fork bracket.



Front edge view, showing one buret in place.



Split and grooved cork, with section of buret.

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about 1.5 cm. of the upper end of the cork will project when snugly pushed down. The corks are bored with borers slightly smaller than the burets they are to carry, and then split longitudinally with a knife into two equal parts. When the two halves of the cork are placed around a buret and wedged snugly down into a hole in the board, the buret will be held securely, but at the same time may be slid up and down much more easily than if held in rubber. There are no screws to rust or strip, and the buret is much easier to insert and remove (through the slot) than in a screw clamp. The burets being held in a regular row at the most convenient intervals, a single stand will hold many more than is convenient with screw clamps.

The arrangement may be improved further by cutting a shallow groove around the cork, before splitting, about 0.5 cm. from its larger end; in this groove are placed two or three light rubber bands. This arrangement adds to the ease of operation, as the cork is held on the buret until deliberately removed, and yet permits the buret to slip up and down easily; one also does not have to be so careful in placing the cork in the slots, as when the bands are not used.

The perforated board is supported by some form of bracket; we use a metal clamp sliding on an ordinary vertical support with a heavy base. A burner fork makes a convenient bracket, it being only necessary to bore two holes horizontally into the back edge of the perforated board at the proper distance apart to receive the prongs of the fork.

The support may also be used with small funnels, and a similar device with larger holes, for larger funnels. The slot in the front makes it possible to remove the funnel from the support without loss while it is still dripping rapidly, the stem of the funnel passing out through the slot while its lower end is kept in the receiving vessel.

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[CONTRIBUTION FROM DRUG DIVISION, BUREAU OF CHEMISTRY, U. S. DEPT. OF AGRICULTURE.]

A CHEMICAL INVESTIGATION OF THE OIL OF CHENOPODIUM.

BY E. K. NELSON.

Received June 9, 1911.

Introduction.

American wormseed oil, official in the United States Pharmacopoeia as *Oleum chenopodii*, is distilled from *Chenopodium ambrosioides*, var. *Anthelmintica*. It is used as a remedy for worms, particularly for Ascarides, which it seems to narcotize so that they can be eliminated by means of a laxative. The larger part of this oil produced in the United

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States is distilled from an herb grown in a section of Carroll County, Md., and is known in the trade as "Baltimore" wormseed oil.

The chemistry of the oil of chenopodium has, until recently, been but little investigated. The first recorded examination of this oil was undertaken by Garrigues,[1] in 1854, who reported the presence of two constituents, one of which he described as a hydrocarbon boiling at 176° C., and the other as a liquid of the formula $C_{10}H_{16}O$.

Kremers[2] examined chenopodium oil in 1907 from the results of which examination he suspected the presence of a most unstable alcohol. Schimmel & Co.,[3] in 1908, reported an extensive investigation of the oil. By fractionating at reduced pressure (the oil explodes on attempting to distil it at atmospheric pressure) they separated a liquid substance, designated by them "ascaridol," which constitutes the major portion of the oil, and to which its peculiar chemical as well as medicinal properties seem to be due. Ascaridole afforded on analysis the formula $C_{10}H_{16}O_2$. It is described as a yellow oil possessing a peculiar, repulsive odor suggesting both camphor and carvone. Toward reagents which would characterize it as an alcohol, an aldehyde, a ketone, or a phenol, ascaridol was found to be absolutely indifferent. Many attempts were made to ascertain the chemical nature of this substance, without results. They found that on heating ascaridole to 150° a molecular rearrangement apparently took place, and that the product of conversion, on combustion, gave values which agreed fairly well with the formula $C_{10}H_{16}O_2$. Ascaridole, when allowed to drop into concentrated sulfuric acid, or when reduced with zinc dust and acetic acid, formed cymene. No cymene was formed from the conversion product, either on treatment with zinc dust and acetic acid or with formic acid.

Besides cymene, Schimmel & Co. found a ketone, probably carvenone, to be formed on reducing ascaridole with zinc dust and acetic acid. The lighter boiling fraction of the oil was found to consist mainly of cymene, mixed, as the optical activity would indicate, with a terpene.

Examination of Authentic Samples.

In October, 1910, authentic samples of chenopodium oil were collected by the writer in the producing section of Maryland for the purpose of making a chemical examination as well as to determin the physical variations. Three samples were collected from a large steam still representing three different crops of the herb. A fourth sample was collected from one of the old-fashioned "pot" stills. The following are the results of a physical examination of these samples:

[1] *Am. J. Pharm.*, 26, 405 (1854).
[2] *Pharm. Rev.*, 25, 155 (1907).
[3] Schimmel & Co., *Report*, April, 1908.

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PHYSICAL TEST ON FOUR AUTHENTIC SAMPLES OF CHENOPODIUM OIL.

Determinations.	Steamed distilled samples. No. 1.	No. 2.	No. 3.	Pot-distilled samples. No. 4.
Specific gravity 25°/25°	0.9691	0.970	0.955	0.9584
n_D at 25°	1.4726	1.4723	1.4726	1.4725
α_D at 25°	—5.4°	—6.2°	—8.8°	—6.3°
Solubility in 70 per cent. alcohol	1 : 3	1 : 3	1 : 7	1 : 6

For a preliminary chemical examination of chenopodium oil a sample was purchased on the market prior to the distillation of the fall crop. This sample, which must have been at least a year old, afforded the following results: Specific gravity (25° C.) = 0.9694; n_D at 20° = 1.4780; α_D at 20° C. = —0.35°; solubility in 70 per cent. alcohol = 1 : 3; acid number = 0; ester number = 5.0.

On fractionating at 8 mm., about 15 per cent. of a hydrocarbon was separated. After distilling this over sodium a pleasant smelling liquid was obtained having a boiling point of 176° C. (766 mm.); a sp. gr. of 0.8513 at 20°; n_D at 20° C., 1.4828; and α_D at 20° C., —18.5°. Cymene was identified in this fraction.

Dextro camphor was identified in the fractions coming over before the ascaridole by means of its semicarbazone and its oxime. The proportion of camphor in the sample was estimated to be at least 4 per cent. This was determined by treating a weighed sample of the oil with semicarbazine hydrochloride and sodium acetate in acetic acid solution, allowing the mixture to stand for some time, and distilling the oil, after freeing from acetic acid, with steam. As camphor semicarbazone is scarcely volatil with steam, it remained behind in a crude form. This was dried on a porous plate and from its weight the amount of camphor was roughly estimated.

The presence of dextro camphor no doubt accounts for the low levo rotation of this sample. Camphor was not found in the fresh authentic specimens, and the question therefore arises whether the camphor may be formed in the oil on aging. The question is to be investigated by an examination of the samples in which no camphor was found after aging a year under varying conditions.

The substance which Schimmel & Co. have designated "ascaridol" was separated as completely as possible by fractionation at 8 mm. Thus purified, it has a constant boiling point, and probably constitutes at least 70 per cent. of the sample.

Boiling point, 8 mm. = 96–97°; specific gravity (20°/20°) = 0.9985; n_D at 20° = 1.4769; α_D at 20° = +0.7°.

Schimmel & Co. found ascaridole to be inactive. The slight optical activity of the ascaridole obtained from this sample is no doubt due to the rather large amount of camphor present, from which the ascaridole was not entirely freed on fractionation.

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Experiments to Determin the Nature of Ascaridole.

The following experiments illustrate the instability of ascaridole: On pouring ascaridole on to mercury, heated to 260°, it inflames. It is decomposed with explosive violence on adding sulfuric, hydrochloric, nitric, or phosphoric acids, and on warming gently with zinc chloride. When heated to 140°, with phthalic anhydride, it is violently decomposed. No phthalic acid ester was found in the reaction product. When heated to near its boiling point, ascaridole decomposes with explosive violence. If dropped into sulfuric acid a combustible, saturated gas is evolved. Treated with acetic anhydride in pyridine solution, it does not react, either at the temperature of the steam bath or at the boiling point of pyridine. On boiling with acetic anhydride, however, some ester is apparently formed, but involving a decomposition of the original material. It affords no oxime and no semicarbazone. Phenyl isocyanate does not react.

On shaking ascaridole with a saturated solution of ferrous sulfate, the temperature rises, a combustible gas is evolved, and basic ferric sulfate is precipitated. This reaction indicates that ascaridole may be an unstable oxide. As the reaction with ferrous sulfate appears to go smoothly and is capable of control, its study seemed to promise some light on the chemical nature of ascaridole, and the following experiments were made:

Experiment 1.—Fifty cubic centimeters of ascaridole were shaken with a saturated solution of ferrous sulfate. The mixture became quite hot, and a small amount of gas was evolved which was collected and found to be combustible. Much basic ferric sulfate was precipitated, and the ascaridole first became colorless and finally quite viscous. Thirty-five cubic centimeters of thick oil were drawn off and the filtered, aqueous solution was extracted with ether. On evaporating the ether a viscous, odorless, water-soluble substance remained, which had a burning taste. Accordingly, the thick oil drawn off at first was shaken out with water, the aqueous extract shaken out with ether, and an additional quantity of the water-soluble substance obtained.

Experiment 2.—Ascaridole, 20 cc., was shaken with ferrous sulfate solution and the entire mixture distilled with steam. The distillate was saturated with sodium chloride and extracted with petroleum ether, the aqueous solution being then distilled into a 50 cc. flask.

The specific gravity (15.6°/15.6°) of distillate is 0.9978, equivalent to 0.57 gram (as ethyl alcohol) or 2.85 per cent. of the ascaridole. The distillate was then fractionated and the concentrated alcohol examined. It gave iodoform in the cold, and on oxidizing with chromic acid afforded acetone, which was identified by means of its condensation product with benzaldehyde, dibenzylidine acetone, melting point 111°–112°. Therefore, isopropyl alcohol is among the products formed from ascaridole on

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treatment with ferrous sulfate; 2 cc. of oil came over with the steam, the greater part being nonvolatil. This was extracted from the retort residue by means of ether and amounted to 15 cc. of a thick, sirupy oil. On acetylation this was found to be alcoholic in nature. The acetyl ester had a decided pennyroyal or pulegone odor, especially upon warming.

Experiment 3.—Treated 20 cc. of ascaridole with ferrous sulfate solution as before, but kept the temperature down by occasional cooling under the tap. Little, if any, gas was evolved and less basic ferric salt was precipitated than in the previous experiments. The ascaridole, as before, became first colorless, then viscous, and part of it went into solution. In all cases the chenopodium odor almost entirely disappeared, and the viscous, soluble substance seemed to be the chief product of the reaction.

Experiment 4.—In order to study further this conversion product of ascaridole, a large amount of the latter was prepared from authentic samples of the oil.

Three hundred cubic centimeters of ascaridole were shaken violently with a nearly saturated solution of 100 grams of ferrous sulfate, keeping the temperature below 35° by occasional cooling. When the temperature ceased to rize and the mixture had become quite viscous, the reaction was considered at an end. The reaction product was recovered from the mixture by means of ether. On shaking it with benzoyl chloride and sodium hydroxide solution (Schotten-Baumann method), a solid crystallin ester was separated. This was filtered off and dried on a porous plate. Recrystallized from alcohol it melted at from 136°–137° C. From this ester the pure alcohol was obtained as an odorless, colorless, viscous oil, which crystallizes on long standing in a vacuum desiccator, the crystals rotating like camphor when dropped on water. The alcohol possesses the following physical characteristics: Boiling point, 271°–272°; melting point, 62.5°–64.0°; specific gravity (20°/20°), 1.0981; n_D at 20° C. = 1.4796; $\alpha_D = 0$; molecular refraction, 48.63 (calculated for a saturated compound with two hydroxyls = 48.65). On analysis the formula was found to be $C_{10}H_{18}O_3$.

Calculated for $C_{10}H_{18}O_3$: C, 64.46, ; H, 9.74.
Found: C, 64.19, 64.20; H, 9.76, 9.66.

This alcohol, as will be shown, contains two hydroxyl groups and therefore is designated as ascaridole glycol.

Monobenzoate of Ascaridole Glycol.

The product of the Schotten-Baumann reaction proved to be a monobenzoate.

0.5183 gram required 3.6 cc. of half-normal potassium hydroxide to saponify = 36.46 per cent. of C_6H_5CO; calculated for $C_6H_5COC_{10}H_{17}O_3$ = 36.21 per cent. C_6H_5CO. Crystallizes from warm alcohol in prisms; melting point = 136°–137°.

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Calculated for $C_6H_5COC_{10}H_{17}O_3$: C, 70.34, ; H, 7.58.
Found: C, 70.62, 70.00; H, 7.16, 7.51.

Dibenzoate of Ascaridole Glycol.

The second hydroxyl group in ascaridole glycol was shown by the preparation of the dibenzoate. This is formed when the glycol is heated with benzoic anhydride to 150° for two hours. The ester recovered was purified by recrystallizing from alcohol, yielding white, glistening needles. Melting point, 116.5°–117.5°.

Calculated for $(C_6H_5CO)_2C_{10}H_{16}O_3$: C, 73.05, H, 6.64.
Found: C, 72.62; H, 6.77.

One gram = 10.21 cc. half-normal potassium hydroxide = 53.62 per cent. C_6H_5CO; calculated for $(C_6H_5CO)_2C_{10}H_{16}O_3$ = 53.28 C_6H_5CO.

The glycol was recovered from this dibenzoate by saponification with potassium hydroxide, unchanged by the conditions of reaction. The boiling and melting points of the recovered glycol were the same as of that prepared through the monobenzoate. A peculiarity of the hydroxyls of ascaridole glycol is shown by the fact that only one reacts under the conditions of the Schotten-Baumann method while both react on heating to 150° with benzoic anhydride.

The Relation of the Glycol to Ascaridole.

Ascaridole glycol does not react with reagents which would characterize it as a ketone or aldehyde, nor does it afford a methoxyl number on subjecting it to the Zeisel method. The third oxygen is therefore, in all probability, an oxide oxygen. In that case ascaridole glycol is quite analogous to pinene glycol, and is the product of hydrating a dioxide. In case ascaridole did not suffer a molecular rearrangement on treatment with ferrous sulfate, or if the reagent merely acted catalytically, resulting in simple hydration, the conclusion would be reached that ascaridole is a glycol anhydride. In such a case it would seem that hydration should result on treatment with very dilute sulfuric acid, or with ferric salts. Both were tried and were found to produce no glycol whatever. As this seemed to indicate that a molecular rearrangement must take place when ascaridole is treated with solutions of ferrous sulfate, attention was then directed to the product of conversion described by Schimmel & Co., which they obtained on heating ascaridole to 150° and which they found to have the same composition as that of the original material. This product was prepared and was found to be the anhydride of the same glycol obtained by the action of ferrous sulfate on ascaridole, for, on treatment with 2 per cent. sulfuric acid, it took up water with rise in temperature, and the hydrate thus formed gave a plentiful yield of the monobenzoate with a melting point of from 136° to 137° when subjected to the Schotten-Baumann reaction. On heating this monobenzoate at

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150° with benzoic anhydride the dibenzoate (melting point 116.5°–117.5°) was obtained.

The method of preparing the conversion product is as follows:

Cymene, 15 cc., was heated in a glycerol bath to 150° and the ascaridole added in 5 cc. portions, not allowing the temperature to rize above 165° until 25 cc. had been added. The mixture was cooled and hydrated by shaking with 100 cc. of 2 per cent. sulfuric acid. To the solution 100 cc. of 20 per cent. sodium hydroxide were added, then 35 cc. of benzoyl chloride. The mixture was shaken until the odor of benzoyl chloride had disappeared, when it was allowed to stand in the refrigerator overnight. Seventeen grams of the monobenzoate were recovered, a yield of 40 per cent. It is probable this yield can be increased by altering the method given.

Therefore, ascaridole suffers a molecular rearrangement with the formation of a glycol anhydride, one oxygen apparently remaining combined with two carbons, as an oxide. By fusion with potassium hydroxide or by boiling with a small amount of sodium, ascaridole glycol is changed, in part, into a substance which oxidizes to a greenish violet color in the air. On acidifying the product from such treatment, adding ferric chloride and distilling with steam a yellow solution comes over, which gives up its color to ether. On shaking the ether with potassium hydroxide solution the latter is colored a beautiful violet. This alkaline solution was acidified, extracted with ether, and on evaporation of the solvent, orange-yellow crystals were obtained (melting point 164°–166°). These crystals afford a purple-red color with concentrated sulfuric acid. The aniline derivative was prepared and crystallized in violet-black needles. This substance therefore is evidently α-hydroxythymoquinone, but the amount recovered was very small.

Oxidation of Ascaridole Glycol.

When ascaridole glycol is oxidized with a neutral solution of potassium permanganate, a difficultly soluble, crystallin acid is formed in preponderating amount. This separates at once in acidifying the concentrated solution filtered from manganese dioxide. The acid is quite soluble in hot water, but is difficultly soluble in cold water. It crystallizes from water in fine glistening needles; melting point, 116.5°–117°; $\alpha_D = 0$ (2 per cent. alcoholic solution).

The formula indicated by analysis is $C_{10}H_{10}O_5$. It is, therefore, isomeric with cineolic acid.

Calculated for $C_{10}H_{10}O_5$:	C, 55.52,	; H, 7.46.
Found:	C, 55.48, 55.28;	H, 7.43, 7.62.

This acid, which is the chief oxidation product, will be designated ascaridic acid. It is dibasic. The silver salt, prepared by precipitation,

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is almost insoluble in water; 0.0637 gram silver salt gave 0.0317 gram Ag = 49.76 per cent.; calculated for $C_{10}H_{14}O_5Ag_2$ = 50 per cent. Ag.

Ascaridic acid reacts neither with hydroxylamine nor with semicarbazine and is evidently, therefore, not a ketonic acid. After boiling with acetic anhydride and rehydrating by boiling with water, the acid was recovered unchanged, which would not have been the case had it contained a hydroxyl group. That it is not a lactone or anhydrid is shown by its behavior on titration.

When heated above its melting point, a lighter boiling substance is formed, which has an odor suggestive of amyl acetate. Methyl heptenone, is, therefore, probably formed, but sufficient material is not available at present to positively identify it by the preparation of derivatives. This acid is probably closely related to cineolic acid, which breaks down into methyl heptenone on dry distillation.

After separating the ascaridic acid, the solution was distilled with steam and a small amount of a mixture of volatil acids recovered. These have not been separated, but apparently acetic and butyric acids are present.

The residue, freed from most of the volatil acid, on cooling, deposited crystallin crusts. This was recrystallized from water and proved to be another acid. It is soluble in hot water, but difficultly soluble in cold water. The crystals are brilliant rhombohedra, melting at 186°–187° (with decomposition).

Calculated for $C_{10}H_{16}O_6$:	C, 51.69; H, 6.95.
Found:	C, 51.00; H, 7.11.

As 0.2066 gram = 17.6 cc. tenth-normal potassium hydroxide, the neutralizing equivalent is 117.3.

The silver salt was prepared by precipitation; 0.3084 gram gave 0.1486 gram Ag = 48.18 per cent.; calculated for $C_{10}H_{14}O_6$, Ag_2 = 48.20 per cent. Ag. The acid, therefore, is dibasic, and its formula is evidently $C_{10}H_{16}O_6$. On heating above its melting point, no odor of methyl heptenone was observed. The amount of these acids available was too small for further examination. Their study is, therefore, reserved for a future communication.

The Chemical Nature of Ascaridole.

The indifference of ascaridole toward reagents, which would characterize it as an aldehyde, ketone, phenol, or alcohol, taken with the fact that it rearranges to form a glycol anhydride, analogous to pinene oxide, seems to warrant the conclusion that it is an unstable dioxide.

Its property of exploding when heated and of giving off a combustible gas under certain conditions (which was also observed by Freer[1] in his

[1] *Am. Chem. J.*, 27, 161 (1902).

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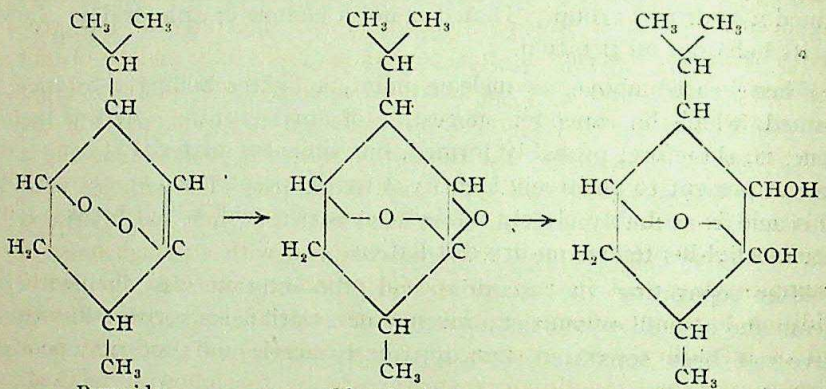
work on acetyl-benzoyl peroxide), as well as the violence of the reaction brought about when treated with ferrous sulfate and other reducing agents, seem to indicate that ascaridole is an organic peroxide.

If so, the following tentative structural formulas, which are intended to show a relationship to hydroxythymoquinone, will indicate the course of the reactions involved.



[CONTRIBUTION FROM THE LABORATORY OF SOIL FERTILITY INVESTIGATIONS.]

DIHYDROXYSTEARIC ACID IN GOOD AND POOR SOILS.[1]

BY OSWALD SCHREINER AND ELBERT C. LATHROP.

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The presence of dihydroxystearic acid in certain infertil soils was reported[2] from this laboratory in 1908 and was followed by a more extensive study of the effects of this substance on plant growth.[3] Since then dihydroxystearic acid has been found so often in the examination of infertil soils brought to the attention of this laboratory as to lead to the conclusion that it is one of the principal factors of infertility in such soils, or at least a contributory factor that is easily determined and thus becomes an indicator of the poor soil conditions which lead to infertility. More accurate knowledge concerning the other organic soil constituents associated with and accumulating under the same conditions as dihydroxystearic acid will doubtless be necessary before this question can be definitly answered, but attention should here be called to the fact that even the knowledge that this one constituent is present leads to a recognition of the fact that poor soil conditions exist and this suggests

[1] Published by permission of the Secretary of Agriculture.

[2] Schreiner and Shorey, THIS JOURNAL, 30, 1599 (1908); "The Isolation of Harmful Organic Substances from Soils," *Bull.* 53, Bureau of Soils, U. S. Dept. Agr. (1909).

[3] Schreiner and Skinner, *Botan. Gaz.*, 50, 161 (1910); "Some Effects of a Harmful Organic Soil Constituent," *Bull.* 70, Bureau of Soils, U. S. Dept. Agr. (1910).

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the practical remedial measures to be employed. The determination of the presence of this compound becomes, therefore, a very valuable and ready means of diagnosing such soil conditions on a limited laboratory sample.

The frequent occurrence of dihydroxystearic acid, together with the fact that it was found in soils unproductive in the field, made it seem highly desirable to test this relationship of soil infertility or low productivity with the presence of this compound more fully and to obtain at the same time an idea of its distribution in the soils of the United States. With this in view, samples were collected in various parts of the United States by field men of the Bureau of Soils. A good sample and a poorer sample of the same soil type were requested. The samples were to be either from the same field, or at least from the same neighborhood and in most cases this request could be complied with although most of the samples thus sent in had no special problem connected therewith. In addition to those collected in this manner, infertil soils with a known record of infertility were examined. These samples of good and poor soils were examined for dihydroxystearic acid by the following method:

Five to ten pounds of soil are extracted for 24 hours with 5–10 liters of 2 per cent. sodium hydroxide solution. The supernatant alkaline extract is siphoned off, made acid with dilute sulfuric acid and filtered. The filtrate is shaken out with ether until nothing more is extracted by ether. The ether extract is allowed to evaporate over a small volume of water and the water solution containing oil and resinous material is boiled vigorously and filtered while hot through a filter wet with hot water. The filtrate containing the dihydroxystearic acid is allowed to cool and is again extracted with ether, evaporated and the water solution boiled and filtered as before. On evaporating the water solution to small volume and allowing it to stand, dihydroxystearic acid will separate out in star-like clusters of white plates or needles which should melt, when pure, at 99°.

A total of 84 soil samples were examined for dihydroxystearic acid; of these 24 were subsoils. Of the total number of samples examined, 27 contained this compound as a constituent part.

The list comprizes a total of 60 surface soils of widely different characteristics, collected in 18 states. They vary from extremely unproductive soils to soils of the highest productivity and represent soils of different origin, different systems of cropping, widely different climatic conditions and of varying texture, from loose sands to plastic clays. Of these soils 33 per cent. showed the presence of dihydroxystearic acid. It was contained in soils under long cultivation, as well as in virgin lands; in soils continually cropped, as well as in soils under permanent sod. This shows that this compound is a common soil constituent and likely

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to be encountered in soil work anywhere. It was found in soils as widely separated as Massachusetts, Texas and Oregon. This at least indicates that there is some force at work which forms this compound in soils everywhere. Its formation or its accumulation is doubtless due to local soil conditions in any one section, but these local soil conditions are not confined to any region of the United States and probably not to any country or continent.

Incidentally in the present investigation it was hoped that the examination of a considerable number of soils would throw further light upon its origin. For this reason as much information concerning the crop history and native vegetation as could be acquired from the respective owners of the soils examined was obtained, but the information thus gained is so meager and imperfect that we hesitate at this time to draw any definit conclusions. It seems, however, that the dihydroxystearic acid is not connected with any specific crop and what information there is points to its association with soil fungi, as already pointed out.[1] The soil conditions under which it is found are generally poor drainage, poor aeration, too great compactness, deficiency in lime, lack of good oxidation, lack of good nitrification, and, as already mentioned, tendency for fungus development and exceptional poorness of crops. While, therefore, all these factors contribute toward the formation or accumulation of dihydroxystearic acid or exist because of its presence, no single one of these factors can, at the present time, be said wholly to explain its origin.

The surface soils examined may be divided into two classes: (1) Good soils, comprizing those of average or high productivity for the soil types represented; (2) poor soils, comprizing those less productive than Class 1, as well as those of undoubted fertility.

GOOD SOILS.

Containing dihydroxystearic acid:

Dunkirk clay, Monroe Co., N. Y.
Orangeburg fine sandy loam, Marshall Co., Texas.

Not containing dihydroxystearic acid:

Amarilla silt loam, Sherman Co., Texas.
Cecil clay, Appling, Ga.
Clarksville gravelly loam, Walker Co., Ga.
Dekalb fine sandy loam, Long Island, Ala.
Dutchess loam, Greenville, N. J.
Hagerstown silt loam, State College, Pa.
Louisa fine sandy loam, Roanoke, Ala.
Madera sand, Fresno, Calif.
Marshall loam, Fargo, N. D.
Norfolk fine sand, Glynn Co., Ga.
Norfolk fine sand, Savannah, Ga.
Norfolk coarse sandy loam, Rockingham, N. C.

[1] *Bull.* 53, Bureau of Soils, U. S. Dept. Agr. (1909).

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Norfolk loam, Mobile Co., Ala.
Norfolk sandy loam, Laurinburg, N. C.
Orangeburg fine sandy loam, Tuscaloosa, Ala.
Orangeburg fine sandy loam, Waynesboro, Miss.
Orangeburg sandy loam, Forrest Co., Miss.
Orono clay, Oldtown, Me.
Peaty soil, Lake Mattamuskeet, N. C.
Cahaba fine sandy loam, Lowndes, Miss.
Sassafras silt loam, Easton, Md.
Stockton, Cal. soil.
Westmoreland silt loam, Clayville, Pa.

Twenty-five of the soils can be classed as good soils, that is, soils of high or average productivity. Of these only two contained dihydroxystearic acid. These were the samples of the Dunkirk clay from New York and the Orangeburg fine sandy loam from Texas. The subsoils of these also contained dihydroxystearic acid. Of the former soil type there was no poorer sample sent in, so no direct comparison of this kind is possible. It is, however, a soil of only fair productivity and the sample may, therefore, not have been so typical of the best fields in this type as should be the case for this classification. It was, however, our judgment, based on the collector's report, that this sample should be classed among the good rather than among the poor soils. With the Texas soil the case is different. Here there is available for comparison a soil sample from an adjoining poorer field of the same type. This poorer field which had not been fertilized and had been so poorly farmed that it was abandoned to native vegetation, contained considerably more than the sample from the better field, which had been well farmed by the growing of truck crops. This is exactly what should be expected in the case of a soil containing this substance when it is improved by manures, fertilizers or thorough cultivation. Ultimately the dihydroxystearic acid should disappear entirely under such conditions.

POOR SOILS.

Containing dihydroxystearic acid:
Baldwin clay, Media Co., Tex.
Boston common soil, 3 samples, Boston, Mass.
Chester silt loam, Philadelphia, Pa.
Clarksville silt loam, Broadhead, Ky.
Clarksville silt loam, Pulaski, Tenn.
Clyde loam, Orleans Co., N. Y.
Durham sandy loam, Clayton, N. C.
Elkton silt loam, Easton, Md.
Frankstown stony loam, Bedford Co., Pa.
Orangeburg fine sandy loam, Marshall, Texas.
Peat, Klamath Marsh, Ore.
Peat, Lanham, Md.
Takoma lawn soil, Takoma Park, Md.
Volusia silt loam, Naples, N. Y.
Woodland soils, 2 samples, Redding, Conn

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Not containing dihydroxystearic acid:

Cecil clay, Appling, Ga.
Cecil sandy loam, Charlotte, N. C.
Dekalb fine sandy loam, Long Island, Ala.
Dekalb silt loam, Ravenwood, W. Va.
Louisa fine sandy loam, Roanoke, Ala.
Madera sand, Fresno, Cal.
Muck, Orleans Co., N. Y.
Norfolk coarse sandy loam, Rockingham, N. C.
Norfolk fine sand, Glynn Co., Ga.
Norfolk fine sand, Savannah, Ga.
Norfolk loam, Mobile Co., Ala.
Orangeburg fine sandy loam, Tuscaloosa, Ala.
Orangeburg fine sandy loam, Waynesboro, Miss.
Orangeburg sandy loam, Forest Co., Miss.
Orono clay, Oldtown, Me.
Cahaba fine sandy loam, Lowndes, Miss.
Sandy loam from a pocoson, Trenton, N. C.

The soils which can be classified as poor soils are 35 in number and comprize those less productive than those considered under the designation of good soils as well as some distinctly infertil soils. Of these poor soils, 51 per cent. contained dihydroxystearic acid.

Ten of the soils had distinct problems of infertility. These are the Volusia silt loam from New York, the three soils from Boston Common, the two soils from Redding, Conn., the Elkton silt loam and the Takoma lawn soil from Maryland, the Chester silt loam from Pennsylvania and the Clarksville silt loam from Tennessee. In every one of these samples of distinctly infertil soils dihydroxystearic acid was found in appreciable amounts, except in the surface soil of the Volusia silt loam, but here it was found in the subsoil.

Deducting these 10 very infertil soils, all of which contained dihydroxystearic acid, from the above 35 poor soils, there remain 25 poor soils about which nothing definit is known excepting that they are relatively less productive than other soils in the same regions. Nevertheless 32 per cent. of these soils contained this soil constituent.

The frequent occurrence of dihydroxystearic acid is of special interest and significance because of its known harmful properties to plants. One-third of all the soils examined showed the presence of this compound. It was found in virgin soils as well as in soils under long cultivation; in soils continually cropped as well as in soils under permanent sod; in soils from the Atlantic coast; in soils from the Pacific coast; and in soils from the Gulf states. This compound is, therefore, a common soil constituent and is likely to be encountered in soils anywhere. Its formation or its accumulation is doubtless due to local conditions in any one section, but these local conditions are not confined to any region of the United States and probably not to any country or continent.

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Judging from the foregoing relationships established by this investigation it would seem that dihydroxystearic acid is either a direct or indirect factor in the low productivity in soils: direct by virtue of its harmful effects on growing crops, indirect as an indicator of other compounds or conditions which cause soil to become less productive and even infertil. It is not possible to state from the data at hand that dihydroxystearic acid is the only factor which contributes to the infertility or unproductivity in those soils in which it was found, for it must be remembered that this is only one of many compounds, both organic and inorganic, harmful and beneficial, which exist in soils, any and all of which play a part in its relative fertility and infertility. It is certain, however, that the determination of even this one constituent leads to a recognition of the kind of infertility in the soils examined and is, therefore, a readily recognized symptomatic factor of poor soil conditions.

BUREAU OF SOILS, WASHINGTON, D. C.

NOTES.

Detection of Gas in Sealed Tube Reactions.—Occasionally organic compounds in sealed tube reactions undergo partial decomposition with liberation of gas. While it may be of no importance to determin the amount of gas, it is sometimes desirable to know just what has been formed. The usual method of placing the substance in a Carius or Volhard tube, which is then heated, drawn to a capillary tip nd sealed, does not permit the satisfactory examination of gas. As soon as the capillary tip is heated in a flame, inside pressure causes the gas to escape. Even if there is no inside pressure, which rarely occurs when gas is formed, it is not practical to connect the capillary tube with an absorption tube or eudiometer.

The following method has proved sa sfactory in such cases: After the substance, with or without a reagent, has been placed in the Carius or Volhard tube, a specially constructed stopcock of the same glass as the tube is sealed to the end. It requires only the slight skill necessary to join two hard glass tubes. The stopcock is open during sealing and a rubber hose, attached to the stopcock and held in the mouth, permits blowing the glass to uniform thickness at the juncture. The seal is then annealed and the stopcock closed. The tube may be heated to any desired temperature, but at temperatures much above 100°, it is a safe precaution, though not absolutely necessary, to wire the stopcock. When the reaction is completed and the tube is cold, connect the latter with the appropriate apparatus and allow the contained gas to escape gradually. To expel more gas, the tube may be heated. When the experiment is finished, the stopcock is removed and used again. Sometimes a tube breaks but not oftener than the ordinary Carius tube. If

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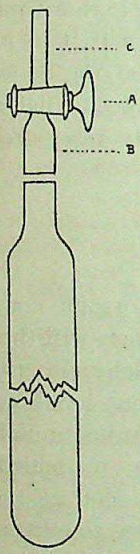
the stopcock is wrapped in a cotton pad, it can often be saved even when the tube breaks. These special stopcocks are not expensive and can be made according to specification by any European dealer in glassware. The style described in this paper was made of so-called "Resistenz" glass and supplied by the firm of C. Desaga, Heidelberg, Germany.

The accompanying sketch and brief description of the dimensions of a stopcock that has proved satisfactory give the necessary details: The stopcocks and tubes, as previously stated, should be of the same glass. Thick-walled Carius tubing is best. The bore of the opening through stopcock *A* is 1.5 mm. in diameter. Stopcock *A* is 2.7 cm. long, its greater diameter at the handle being 1 cm. and its lesser diameter 8 mm. The larger tube *B* should have the same internal diameter as the Carius or Volhard tube to which it is sealed. Its internal diameter is 1.3 cm., wall-thickness 2 mm., and it extends 7 cm. from the stopcock box. The smaller tube *C* is 4 mm. in internal diameter and extends 4 cm. from the stopcock box. The best lubricant for the stopcock is graphite.



As an example of a use of this method in sealed-tube work, the following case may be cited. An organic compound heated for a long time with a volatil reagent slowly gave off acetylene gas. To prove conclusively that such a reaction took place, the experiment was conducted as described above. Upon opening the stopcock and passing the contained gas through ammoniacal cuprous chloride solution, copper acetylide was formed. This reaction would not have taken place in an open tube. In an ordinary sealed tube the recognition of acetylene would have been difficult, if not impossible. The above method settled the question beyond doubt.

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NEW BOOKS.

A Concise History of Chemistry. By T. P. HILDITCH. Pp. ix+263 (sixteen diagrams). 1911. New York: D. Van Nostrand Co. 5×8 in. Cloth, $1.05.

This volume aims to give a brief outline of the entire history of chemistry from earliest times to the present day. The treatise contains eleven chapters which are devoted to the beginning of the science, inorganic compounds, organic compounds and their reactions, chemistry of plant and animal life, applications of chemistry to manufactures, and physical chemistry. There is an appendix containing a biographical index of chemists and a chronological summary of chemical events of outstanding interest.

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In the preface it is stated that the book is designed more especially for those students whose interest is stimulated in the historical aspect of the science by the inclusion of "Historical Chemistry" in the syllabus of examinations which concern them. As an aid in reviewing the history of chemistry preparatory for an examination in the subject, the volume will doubtless be of service; but as a source of studying the development of chemistry in order to obtain a clearer insight into the fundamentals of the science and an inspiration for research, the treatment is quite inadequate. There seem to be but few errors in the book, but the treatment is often so very brief that clear, accurate conceptions are not conveyed to the reader.

The mechanical features of the volume are quite acceptable and the price is low.

L. KAHLENBERG.

Chemistry for Beginners. Vol. I. Inorganic. By EDWARD HART, PH.D. Fifth Edition, Revised and Enlarged. With 78 illustrations and 2 plates. Published by the Chemical Publishing Co., Easton, Pa. 1910. Pages viii+214. Price, $1.00.

That this text has reached its fifth edition is evidence of the fact that it has found a place among the successful texts of elementary chemistry. It is true to its name—"Chemistry for Beginners." The book is small, 12mo., and the treatment of the subject confined to 207 pages, including 204 experiments and 78 illustrations. The author believes, however, that it "will form a sufficient introduction to qualitative analysis." The order in which the subjects are discussed is similar to that commonly adopted, but the treatment is of necessity very brief.

WM. MCPHERSON.

Qualitative Chemical Analysis. Second Edition, Revised. By OLIN FREEMAN TOWER, Professor of Chemistry in Western Reserve University. Philadelphia, Pa.: P. Blakiston's Son & Co. 1911. xiii+84 pages. Price, $1.00.

A brief outline of qualitative analysis well arranged and clearly presented. For theoretical discussions the student is referred to Alexander Smith's "General Chemistry for Colleges" and also to Edwin Lee's "Experimental Chemistry." For complete and detailed discussions, however, the student might well be referred to Alexander Smith's "General Inorganic Chemistry." Throughout the introductory considerations the use of heavy and light arrows, by way of indicating the specific tendency of an electrolyte to enter into ionic or non-ionic form, is exceedingly helpful. The laboratory directions are brief but explicit and include in this edition a few additional methods of separation, such for example as the nitroso-beta-naphthol method for cobalt and nickel. The solubility table is also considerably enlarged over that in the first edition.

WILLIAM J. HALE.

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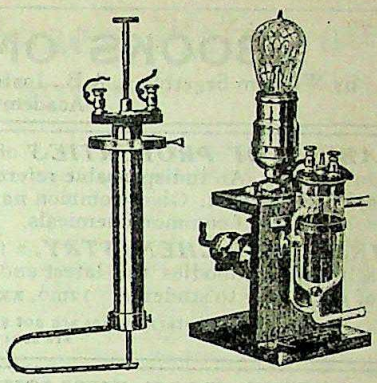

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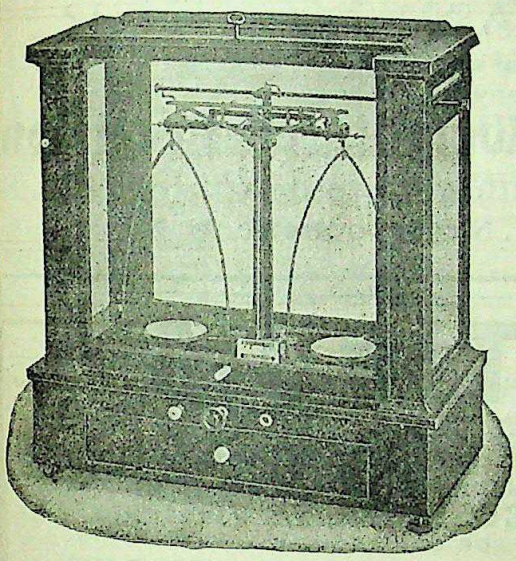

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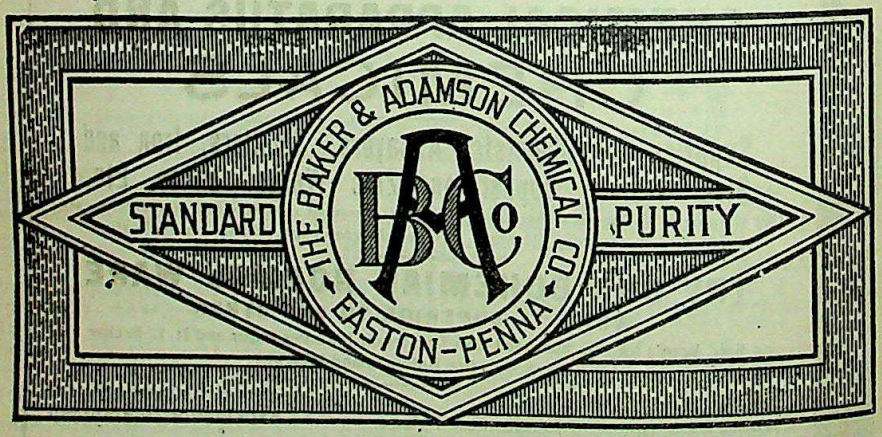

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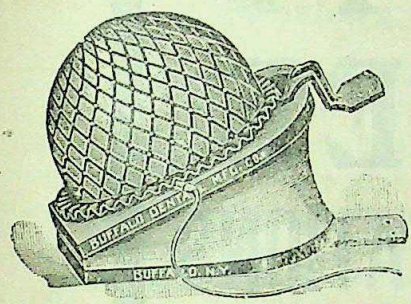

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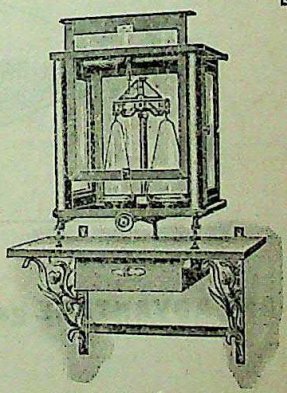

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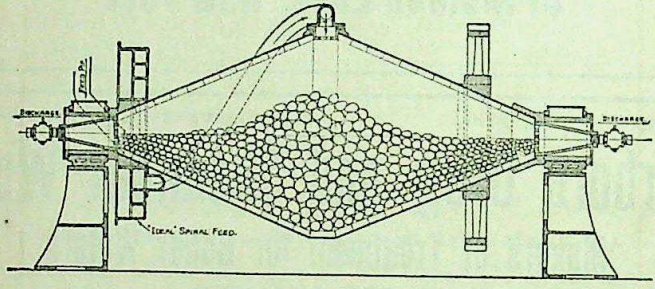

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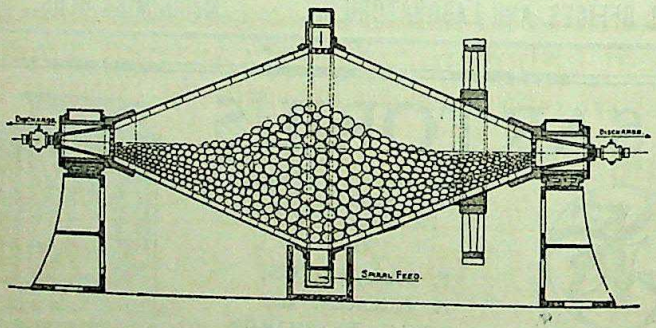

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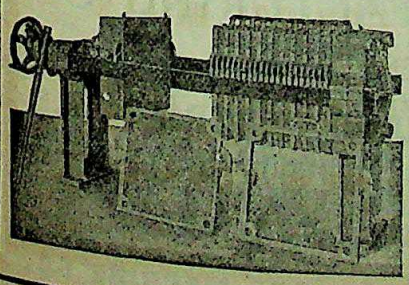

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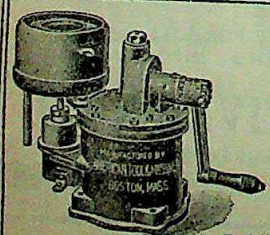

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THE CONDUCTIVITY AND IONIZATION OF A PENTA- AND A HEXA-IONIC SALT.

BY ARTHUR A. NOYES AND ROBERT H. LOMBARD.

Received July 3, 1911.

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1. Purpose of the Investigation.

A study of the existing conductivity data relating to salts of poly-ionic, multivalent types has led to the conclusion that the change of the ionization (γ) of such salts (as derived from the conductance-ratio Λ/Λ_0) with the concentration (C) may be expressed by the same function as holds true in the case of uni-univalent salts, in spite of the fact that the mass-action law requires a different function.[1] Thus the function $C(1-\gamma) = K(C\gamma)^n$ holds true approximately for almost all salts of whatever type investigated, when to the exponent n are given values which vary only between the limits of 1.40 and 1.55, although the mass-action law requires a value of n equal to the number of ions into which the salt dissociates—thus 2 for di-ionic salts, 3 for tri-ionic salts, etc. The further conclusions have also been drawn, (1) that the degree of ionization (γ) at a given (small) concentration is not far from the same for almost all salts of the same type,

[1] See THIS JOURNAL, 30, 343 (1908); 31, 1000 (1909).

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and (2) that the un-ionized fraction $(1 - \gamma)$ at any definit (small) molal concentration is roughly proportional, in the case of different types of salts, to the product of the valences v_1, v_2 of the two ions of the salt;[1] that is, $(1 - \gamma) = K(v_1 v_2)$ for a definit value of C, K having a value of about 0.13 at 0.05 molal at 18° or 25°.

The number of the salts yielding more than three ions that have been accurately investigated in these directions is, however, very small.[2] This investigation was therefore undertaken, with the aid of a grant from the Carnegie Institution of Washington, in order to test further the applicability of these principles in the case of salts of high valence types. Two salts, with valence-products 1×5 and 1×4, respectively, were employed; namely the penta- and tetra-sodium salts of benzene-pentacarboxylic acid, $C_6H(COOH)_5$. Incidentally the conductance of the acid itself was also measured.

The conductance of the two salts were measured at 0°, 25°, and 50° at the concentrations 0.2, 0.6, 2, 6, 20, and 50 milliformal.[3] The conductances of the acid were measured only at 25°, at the concentrations 0.6 to 20 milliformal. In addition to the conductance measurements, the viscosities of the salt solutions were determined. From these conductance and viscosity data the ionization (γ) of the salts was calculated by means of the equation $\gamma = \mu\eta/\mu_0\eta_0$ in which η and η_0 are the viscosities of the solution and of pure water, and μ and μ_0 are the formal conductances at the concentration in question and at zero concentration, respectively.

The density of all solutions was also determined, in order to compute the volume concentration of the solutions from their composition by weight, since for greater convenience and accuracy they were all made up by weighing.

Incidentally it was also necessary to make sure that the degree of hydrolysis of the penta-sodium salt and the hydrogen ionization of the tetra-sodium salt were not large enough to influence appreciably the conductance. This was done by the use of phenolphthalein and paranitro-

[1] THIS JOURNAL, 30, 348 (1908); 31, 1003 (1909).

[2] Noyes and Johnston (THIS JOURNAL, 31, 997–1006 (1909)) studied at temperatures from 0° to 100° or above, potassium citrate and lanthanum nitrate as examples of the uni-trivalent type, potassium ferrocyanide as an example of the uni-quadrivalent type, and barium ferrocyanide, calcium ferrocyanide, and lanthanum sulfate as examples of still higher types. Whetham (*Z. physik. Chem.*, 33, 351 (1900)) studied potassium ferricyanide at 0° up to 0.01 normal. Ostwald (*Ibid.*, 2, 903 (1888)) and Walden (*Ibid.*, 8, 446 (1891)) have investigated at 25° the sodium salts of several polybasic organic acids.

[3] Concentrations expressed in formula weights per liter are designated throughout this article as *formal concentrations*, in accordance with the practice followed in this laboratory.

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phenol respectively, with the aid of the theory of indicators.[1] It was estimated in this way that at 25° the hydroxyl-ion concentration in a 0.02 formal solution of the penta-sodium salt prepared, like that used for the measurements, by titrating the acid with sodium hydroxide with phenolphthalein to a faint red color was 2×10^{-7}; and that the hydrogen-ion concentration in a 0.02 formal solution of the tetra-sodium salt is 3×10^{-6} mols per liter. The hydrogen-ion concentration in solutions of the tetra-sodium salt at 25° was estimated to be 3×10^{-6} mols per liter at all concentrations.[2] Neither of these quantities is large enough to give rise to a conductance forming an important part of the total conductance, even in the case of the most dilute solutions investigated.

2. Description of the Conductivity Apparatus and Method.

Conductivity Apparatus.—The conductances at all three temperatures were measured in two glass cells of the pipet type.[3] Cell "A" was designed for measuring concentrated solutions and was used for the concentrations above 2 milliformal. Cell "B" was designed and used for the solutions at or below 2 milliformal.

The conductances were measured on a slide-wire bridge of the roller type.[4] The slide wire was calibrated both by the method of Strouhal and Barus,[5] and by the use of resistance boxes.[6] The resistance coils of the bridge were also calibrated. The resistance of the leads, which

[1] See THIS JOURNAL, 32, 820 (1909).

[2] The estimates were based on the following experiments: 10 cc. of a paranitrophenol solution were added to 70 cc. of a 0.022 formal solution of the tetra-sodium salt, Na_4HA, and the volume of the same paranitrophenol solution which had to be added to 80 cc. of dilute NaOH to give the same color was determined. This volume was found to be 0.30 cc., showing that the indicator was 3.0% transformed into its colored salt in the solution of the salt. From this we find, taking the constant K_I of the indicator-acid (HIn) as 9×10^{-8}, $C_{H^+} = K_I \frac{C_{HIn}}{C_{In}} = 9 \times 10^{-8} \times \frac{97.0}{3.0} = 2.9 \times 10^{-6}$. Entirely similar experiments were made with 0.022 formal solutions of ($0.97\ Na_4HA + 0.03Na_5H_2A$) and of ($0.97Na_4HA + 0.03Na_5A$). In the former of these solutions the fraction of the indicator transformed was found to be 2.6%, from which C_{H^+} is calculated to be 3.4×10^{-6}. In the latter solution the fraction transformed was found to be 3.4%, from which follows $C_{H^+} = 2.5 \times 10^{-6}$. The experiments with the penta-sodium salt were made with phenolphthalein in a similar way. The addition of enough NaOH to correspond to $Na_5A + 0.01NaOH$ only increased C_{OH^-} from 2×10^{-7} to 1×10^{-6}. It is to be noted that the solutions tested were those prepared by titration and did not contain exactly equivalent quantities of sodium and the acid constituent

[3] THIS JOURNAL, 31, 732 (1909).

[4] Kohlrausch and Holborn, *Das Leitvermögen der Elektrolyte*, pp. 41–42.

[5] Ostwald-Luther, *Phys. Chem. Messungen.*, 3rd Ed., p. 408 (1910).

[6] *Loc. cit.*, p. 407.

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was 0.036 ohm in the 0° and 50° measurements and 0.021 in the 25° measurements, was corrected for.

Thermostats.—The 0° bath was a well-lagged cylindrical metal vessel filled with a mixture of distilled water and a large proportion of crushed ice. It was not found necessary to stir it, as its temperature remained constant within 0.02°. At 25° and 50° electrically heated thermostats, provided with efficient stirrers, were used. The variations of temperature from 25° or 50° never exceeded 0.02°.

Thermometers.—Three thermometers, graduated in tenths of a degree, were used—one for each of the three temperatures. They were calibrated, in the position in which they were used, by comparison with a standard Baudin thermometer which had been certified by the Bureau of Standards at Washington.

Conductance-Capacity of the Cells.—The conductance-capacities of both the cells were determined by measuring in them the conductance at 18° of a 0.01 normal potassium chloride solution, freshly prepared by dissolving, in accordance to the specifications of Kohlrausch,[1] 0.7456 g. (weighed in air) of recrystallized potassium chloride in one liter of solution at 18°. The specific conductance of this solution was taken as 0.0012243.[2]

The conductance-capacity was determined before and after each series of dilutions of a solution, eleven times in all. The values remained constant within 0.1 per cent. throughout the work. Those used were 4.393 for cell "A" and 0.07670 for the cell "B."

The Water Correction.—The specific conductance of the water from which the more dilute solutions were prepared was measured at 25° and subtracted from that of the solution. The average values in reciprocal ohms of the specific conductance of the water (after it had been shaken in the bottle in which the solution was to be made) are as follows: 0.4×10^{-6} at 0°; 0.8×10^{-6} at 25°; and 1.2×10^{-6} at 50°. The percentage correction was very small, except in the case of the 0.0006 formal salt solution, where it amounted to 0.2 to 0.3 per cent. and in the case of the 0.0002 formal solutions where it amounted to 0.4 to 0.7 per cent.

Procedure.—The measurements at 0°, 25°, and 50° were always made in this order in immediate succession, with the same filling of the cell. After the 50° measurement, the solution was brought back to 25° and then to 0°, and again measured at these temperatures. The return values were usually identical with the original values, the only exception observed being that the conductance of the 0.0002 formal solution of the penta-sodium salt was 0.1 per cent. to 0.2 per cent. larger after

[1] *Wissen. Abhd. Phys.-techn. Reichsanstalt*, 3, 180 (1900).
[2] *Loc. cit.*, p. 210.

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the solution had been heated to 50°. The conductance of the solutions was usually measured on the day after they were prepared.

3. Preparation of the Substances and Solutions.

Benzenepentacarboxylic Acid.—The benzenepentacarboxylic acid used in this investigation was furnished us by Professor John E. Bucher, of Brown University, for which we wish to express to him our great indebtedness. It was prepared by him by a process of which he will later publish a description. It had been recrystallized three times from cold water, and then had been dried to constant weight in a room at 5°. This treatment was to assure the production of the penta-hydrate, $C_6H(COOH)_5.5H_2O$. He found by titration, using phenolphthalein as an indicator, a molecular weight of 388.1, the theory for $C_6H(COOH)_5.5H_2O$ being also 388.1. He states also that heating at about 95° in a steam-heated Victor Meyer bath caused a loss of weight of 23.16 per cent., the water content calculated from the above formula being 23.21 per cent.

As a stock solution from which all other solutions were made, there were prepared about 250 cc. of an approximately 0.1 formal solution of the acid. For this purpose a portion of the acid was dried to constant weight at 130°, was accurately weighed, and was then washed into a weighed 250 cc. "Resistenz-Glas"[1] bottle with approximately the desired volume of conductivity water, and the bottle and solution were weighed. The concentration of this solution was computed to be 0.5551 equivalents of acid per 1000 grams of solution. Three titrations against a standard (approximately 0.1 normal) solution of Merck's sodium hydroxide with phenolphthalein gave the values 0.5540, 0.5540, and 0.5544 equivalent per 1000 grams of solution. The mean value 0.5546 was employed as the basis of the concentrations of the acid solutions whose conductance was measured.

A portion of this stock acid solution was diluted to a concentration of 0.1 equivalent of acid per 1000 grams of solution. From this solution the three more dilute solutions whose conductance was measured were prepared by weighing a portion of the stock solution into a carefully cleaned "Resistenz-Glas" bottle, adding the calculated weight of conductivity water and weighing again. Duplicate solutions were prepared in all cases, except for the conductance measurements with the 0.05 formal solutions of the salts and the 0.02 formal solution of the acid, and for the viscosity measurements with the salts.

All the standard sodium hydroxide solutions used in the work were titrated against a hydrochloric acid solution, the strength of which had been determined gravimetrically by precipitation as silver chloride.

[1] These bottles, made by Greiner and Friedrich, of Stützerbach, Germany, were used throughout the work.

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The international atomic weights of 1911 were used throughout the work. Weights were not reduced to the vacuum standard.

Penta-sodium Benzenepentacarboxylate.—This salt was prepared in solution by exactly neutralizing with the aid of phenolphthalein[1] a portion of the stock solution of the acid with a standard (approximately 0.6 normal) solution of sodium hydroxide, prepared as described below. This stock solution of the penta-sodium salt was diluted, by weight, first to 0.05 formal, and then to 0.02 formal; and from this last solution all the other more dilute solutions were made.

Tetra-sodium Benzenepentacarboxylate.—The tetra-sodium salt was made in solution by adding to a weighed portion of the stock solution of the acid, contained in a 250 cc. bottle, 80 per cent. of the weight of freshly prepared standard sodium hydroxide solution found to be necessary for complete neutralization. The solution was diluted as in the case of the penta-sodium salt.

Sodium Hydroxide Solutions.—In order to eliminate carbonate, the sodium hydroxide solutions used for making the sodium salts of the acid were prepared by decomposing with water electrolytically prepared sodium amalgam. In detail the process was as follows: About 200 cc. of a saturated solution of pure sodium carbonate were electrolyzed with a current of 0.5 ampere for about 48 hours in a 300 cc. separatory funnel surrounded with ice and containing 60–100 cc. of pure mercury as cathode and a platinum wire as anode. The amalgam was then allowed to run slowly into a 500 cc. bottle (filled with air free from carbon dioxide), provided with a soda-lime tube and a delivery tube. Fresh conductivity water was then forced into it through the delivery tube. A platinum tube standing upright in the amalgam served to accelerate its decomposition, which is otherwise slow at room temperature. The first sodium hydroxide solution, from which was made the solution of the penta-sodium salt used in the conductivity work, developed, after standing, a very slight turbidity, which was apparently due to the bottle having been attacked by the solution. Therefore, in making the later solutions, the interior of the bottle was coated (at 225°) with paraffin which had been filtered, boiled with sodium hydroxide solution, and then washed with hot water until free from alkali. Altogether, three solutions were made by this method, one for the conductance measurements with the penta-sodium, and one for those with the tetra-sodium salt, and a third for the viscosity measurements with both salts.

[1] Only 0.05 cc. of the phenolphthalein solution was used, and this had been especially prepared by dissolving 0.2 g. purified phenolphthalein in 50 cc. of a 50 per cent. mixture of conductivity water and pure alcohol. Four drops of this solution increased the specific conductance of conductivity water only from 0.8×10^{-6} to 1.2×10^{-6} so that its effect upon the conductance of the solutions was negligible.

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4. The Densities and Volume-Concentrations of the Solutions.

The densities of the solutions, which were determined in a Sprengel-Ostwald 10 cc. picnometer, are given in Table I. The values are ratios of the densities to that of water at 4°. The numbers in the first column show the number of milliformula-weights per 1000 grams of solution.

TABLE I.—DENSITIES OF THE SOLUTIONS.

Comp. by wt.	Penta salt at 0°.	Tetra salt at 0°.	Acid at 25°.	Penta salt at 25°.	Tetra salt at 25°.	Penta salt at 50°.	Tetra salt at 50°.
50	1.0172	1.0152	.....	1.0136	1.0116	1.0041	1.0019
20	1.0067	1.0060	1.0000	1.0037	1.0029	0.99440	0.99369
6	1.0020	1.0017	0.99804	0.99910	0.99890	0.99002	0.98978
2	1.0006	1.0005	0.99740	0.99781	0.99772	0.98871	0.98864
0	0.99987	0.99987	0.99707	0.99707	0.99707	0.98807	0.98807

Table II contains in the last seven columns the values of the volume-concentrations, expressed in milliformula-weights per 1000 cc. of solution, computed from the densities and the compositions by weight given in Table I and in the first column of Table II:

TABLE II.—FORMAL CONCENTRATIONS CORRESPONDING TO COMPOSITIONS BY WEIGHT.

Comp. by wt.	Penta salt at 0°.	Tetra salt at 0°.	Acid at 25°.	Penta salt at 25°.	Tetra salt at 25°.	Penta salt at 50°.	Tetra salt at 50°.
50.0	50.86	50.76	....	50.68	50.58	50.21	50.11
20.0	20.14	20.12	20.00	20.08	20.06	19.89	19.87
6.0	6.012	6.010	5.988	5.994	5.994	5.940	5.938
2.0	2.002	2.002	1.995	1.996	1.995	1.977	1.977
0.6	0.6000	0.5998	0.5982	0.5982	0.5982	0.5928	0.5928
0.2	0.2000	0.2000	....	0.1994	0.1994	0.1976	0.1976

5. The Specific Conductance Data.

Table III contains the values of the specific conductance in reciprocal ohms. In deriving these values, the conductance of the solution meas-

TABLE III.—SPECIFIC CONDUCTANCE $\times 10^4$.

Comp. by wt.	Penta salt at 0°.	Tetra salt at 0°.	Acid at 25°.	Penta salt at 25°.	Tetra salt at 25°.	Penta salt at 50°.	Tetra salt at 50°.
50.0	71.62	61.31	...	140.8	121.2	218.3	190.3
20.0	33.92	28.79	55.21	66.14	56.54	102.1	88.65
	33.92	28.81	...	66.11	56.54	102.2	88.61
6.0	12.57	10.44	22.70	24.40	20.41	37.78	32.07
	12.56	10.44	22.72	24.39	20.41	37.75	32.07
2.0	5.022	4.029	9.681	9.761	7.904	15.17	12.46
	5.020	4.029	9.689	9.765	7.908	15.17	12.45
0.6	1.773	1.364	3.674	3.456	2.684	5.427	4.253
	1.774	1.364	3.670	3.457	2.684	5.427	4.254
0.2	0.6475[1]	0.4900	.....	1.270[1]	0.9636	2.004[1]	1.532
	0.6518	0.4899	.....	1.276	0.9633	2.017	1.532
	0.6496	.....	.....	1.276	.....	2.017	.....
	.....	.....	.....	1.276	.....	.....	.....

[1] These values were rejected in deriving the final value.

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ured in the cell (corrected for errors in the bridge and for the resistance of the leads) was multiplied by the conductance-capacity of the cell, and from this product the specific conductance of the water was subtracted. When more than one value is given at a concentration, it represents the results from two or more independently prepared solutions. The general agreement between such results shows that the conductance measurements were reproducible within 0.1 per cent. except in the case of the 0.0002 formal solutions, where the large water correction and the sensitiveness of contamination make the results uncertain by 0.2–0.3 per cent.

6. Values of the Formal Conductance.

The formal conductance[1] (μ) at each concentration and temperature was obtained by dividing the average of the specific conductance values $\times 10^4$ given in Table III by 10 times the corresponding formal concentration given in Table II.

The formal conductance (μ_0) at zero concentration was computed by the method usually employed in this laboratory;[2] namely, by plotting $1/\mu$ against $(C\mu)^{n-1}$ with various values of the exponent n and extrapolating to zero concentration by means of the curve that is most nearly a straight line at the three smallest concentrations.

The values of the formal conductance obtained in this way are given in Table IV:

TABLE IV.—VALUES OF THE FORMAL CONDUCTANCE.

Comp. by wt.	Penta salt at 0°.	Tetra salt at 0°.	Acid at 25°	Penta salt at 25°.	Tetra salt at 25°	Penta salt at 50°	Tetra salt at 50°.
50.0	140.8	120.8	...	277.9	239.6	434.8	379.9
20.0	168.5	143.2	276.1	329.5	281.9	508.0	446.0
6.0	209.1	173.7	379.2	407.0	340.6	636.0	540.0
2.0	251.0	201.4	485.5	489.3	396.3	767.0	630.0
0.6	295.7	227.4	614.0	578.0	448.7	915.5	717.5
0.2	325.4	245.1	...	640.0	483.2	1020.5	775.0
0.0	371	276	...	751	536	1222	868

7. Relative Values of the Conductances of the Two Anions.

By subtracting from the formal conductances of the penta-sodium and tetra-sodium salts at zero concentration the conductance of five and four equivalents of sodium-ion[3] respectively, the following values are obtained for the formal conductance of the ions $(C_{11}HO_{10})^V$ and $(C_{11}H_2O_{10})^{IV}$.

[1] By "formal conductance" is meant the conductance between electrodes one centimeter apart of that quantity of the solution which contains one formula-weight of the salt.

[2] See Noyes and Johnston, THIS JOURNAL, 31, 994 (1909).

[3] The equivalent conductance of sodium-ion being taken, in accordance with the calculations of Johnston (THIS JOURNAL, 31, 1015 (1909)), as 26 at 0°, 51 at 25°, and 82 at 50°.

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	0°.	25°.	50°.
$(C_{11}HO_{10})^{V}$	241	496	812
$(C_{11}H_2O_{10})^{IV}$	172	332	540
Ratio	1.40	1.49	1.50

Since these two ions differ in molecular composition by only one hydrogen atom, it might be expected (assuming equal hydration) that they would meet with nearly the same frictional resistance to their motion through the solution. Their linear velocities would then be proportional to the electric force acting upon them and therefore to the charge upon them, so that the ratio of their velocities would be 5 : 4. Since the relative quantities of electricity transported by one formula-weight of the two ions are also as 5 : 4, the ratio of their formal conductances would be $5^2 : 4^2$ or 1.56. This is in fact not very different from the actual values of the ratios at 25° and 50°. Similar relations were found to hold true by Abbott and Bray[1] for the ions of phosphoric acid and of pyrophosphoric acid.

8. The Ionization Relations of Benzenepentacarboxylic Acid.

An idea of the ionization relations of the benzenepentacarboxylic acid at 25° may be obtained by comparing its formal conductances given in Table IV for the various concentrations with the conductance values that would correspond to complete ionization of the first hydrogen and of the second hydrogen of the acid. These latter values (taking μ for H^+ = 350, μ for $C_{11}H_5O_{10}^-$ = 21, and μ for $C_{11}H_4O_{10}^=$ = 84) are 371 and 784, respectively. It will be seen that the actual conductance at 0.006 formal corresponds approximately with that for complete ionization of the first hydrogen, and that that at 0.0006 formal is nearly 80 per cent. of that corresponding to complete ionization of two hydrogens. These results show therefore that the acid remains a fairly strong one until at least two of its five hydrogens have been neutralized by a base.[2]

9. The Viscosity Measurements.

Apparatus and Method.—The viscosities of the solutions were measured in a viscosimeter, similar to that described by Ostwald and Luther.[3] The volume of the upper bulb was about 13 cc. and the diameter and length of the capillary tube were 0.052 and 20 cm., respectively. The time of flow of water at 25° was 514 seconds.[4]

[1] THIS JOURNAL, 31, 762 (1909).

[2] It may be incidentally mentioned that the change of conductance of the acid between the concentrations studied (0.0006 to 0.02 formal) is satisfactorily expressed by the function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^{1.50}$, Λ_0 being considered merely as an arbitrary empirical constant.

[3] *Phys.-Chem. Messungen*, 3rd Ed., p. 231 (1910).

[4] For a capillary tube of these dimensions, the limiting velocity of flow, which cannot be exceeded without introducing an error of 0.1 per cent., due to the eddying of the liquid in the capillary, is, according to a formula deduced by Grüneisen (*Wissens.*

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The viscosimeter was wired firmly to a vulcanite plate, which was supported from the side of the thermostat through a ball-and-socket joint, and was therefore capable of adjustment in all directions. A plummet attached to the vulcanite plate made it possible to bring the viscosimeter always to exactly the same vertical position. The viscosimeter was filled from a 25 cc. pipet, into which the solution had been forced through a small asbestos filter, which removed any particles suspended in the solution. The time of flow was measured by a stop-watch with a dial divided into fifths of a second, nine to sixteen check measurements being made with each filling.

The Viscosity Data.—In Table V are presented the results of the viscosity measurements. The first column contains the composition of the solution by weight, expressed in milliformula-weights per 1000 grams of solution. The second column contains the time of flow in seconds; and the third, the average deviation of the individual values from the means. In the fourth column are given separate values (corresponding to different fillings of the apparatus with the same solution), and in the fifth column average values of the ratio (η/η_0) of the viscosity of the solution to that of water at the same temperature. These values were computed by the formula $\eta/\eta_0 = td/t_0d_0$, where d and d_0 are the densities

TABLE V.—THE VISCOSITY DATA.

Tetra-sodium Salt.

Temp.	Comp. by wt.	Time of flow.	a. d.	Viscosity-ratio. Separate values.	Viscosity-ratio. Mean value.
25°	50.0	546.08	±0.30	1.0772	1.0772
	20.0	529.01	±0.35	1.0345	
		528.49	±0.56	1.0335	1.0340
	6.0	519.86	±0.43	1.0117	
		519.93	±0.37	1.0118	1.0118
	2.0	517.17	±0.38	1.0063	
		516.08	±0.22	1.0042	1.0053
	0.6	516.13	±0.32	1.0035	
		515.32	±0.60	1.0019	1.0027
	0.0	514.34[1]	±0.27	1.0000	1.0000
0°	50.0	1091.2	±0.6	1.0762	1.0762
	20.0	1055.7	±0.3	1.0317	1.0317
	0.0	1029.5	±0.6	1.0000	1.0000
50°	50.0	341.18	±0.38	1.0767	1.0767
	0.0	321.30	±0.26	1.0000	1.0000

Abh. Phys.-Techn. Reichsanstalt, 4, 165 (1904)) 20 centimeters per second—thus much larger than that in our experiments, which was 12 centimeters per second. The accuracy of the viscosimeter was also tested by measuring in it, at 18°, the velocity of a normal sodium chloride solution, the value being found to agree with that given by Grüneisen within 0.1 per cent.

[1] Mean of five measurements.

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TABLE V (*Continued*).
Penta-sodium Salt.

Temp.	Comp. by wt.	Time of flow.	a. d.	Viscosity-ratio. Separate values.	Viscosity-ratio. Mean value.
25°	50.0	551.34	±0.37	1.0897	1.0897
	20.0	530.27	±0.26	1.0378	
		530.68	±0.22	1.0386	1.0382
	6.0	520.89	±0.48	1.0148	
		520.94	±0.40	1.0149	1.0149
	2.0	516.49	±0.46	1.0049	
		517.16	±0.34	1.0062	1.0056
	0.6	515.79	±0.30	1.0028	
		516.12	±0.22	1.0035	1.0031
	0.0	514.34[1]	±0.27	1.0000	1.0000
0°	50.0	1099.7	±0.6	1.0867	1.0867
	0.0	1029.5	±0.6	1.0000	1.0000
50°	50.0	343.81	±0.19	1.0874	1.0874
	0.0	321.30	±0.26	1.0000	1.0000

of the solution and of water, as given in Table I, and t and t_0 are the times of flow of the solution and of water, respectively.

10. Values for the Ionization of the Two Salts.

From the values of the formal conductance (μ) given in Table IV and of the viscosity (η) given in Table V, the values of the ratio $\mu\eta/\mu_0\eta_0$ for the two salts were calculated.[2] This ratio will be called the ionization (γ); but it should be noted that it is a true measure of ionization only on the assumption that the intermediate ions do not exist. The values so obtained are given in Table VI:

TABLE VI.—IONIZATION VALUES.

Comp. by wt.	0°. Penta salt.	0°. Tetra salt.	25°. Penta salt.	25°. Tetra salt.	50°. Penta salt.	50°. Tetra salt.
50.0	41.3	47.0	40.3	48.1	38.7	47.1
20.0	47.2	53.4	45.6	54.3	43.1	53.1
6.0	57.2	63.6	55.0	64.2	52.8	62.9
2.0	68.1	73.2	65.5	74.2	63.1	72.9
0.6	80.0	82.5	77.2	83.9	75.1	82.9
0.2	87.8	88.7	85.2	90.1	83.5	89.3
0.0	100.0	100.0	100.0	100.0	100.0	100.0

11. Change of Ionization with the Concentration and Temperature.

In order to determine how the ionization (γ) of these salts varies with the concentration, values of $1/\gamma$ were plotted against $(C\gamma)^{n-1}$ with values of n varying between 1.20 and 1.55 inclusive. It was found that with any one value of the exponent the graph was approximately linear

[1] Mean of five measurements.

[2] At 0° and 50° the viscosity-ratio was taken the same as at 25° except for the stronger solutions with which direct measurements were made at 0° and 50°.

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only through a definit interval of concentrations, showing that no exponential function of the form $C(1-\gamma) = K(C\gamma)^n$ satisfactorily expresses the change of ionization with the concentration. The value of the exponent n at 25° giving a linear graph for the concentration-intervals 0.2 to 2.0 milliformal is 1.55 for both salts, and that for the concentration-interval 2 to 20 milliformal is 1.20 for both salts. The value for the lower concentration-interval is about the same as that previously found for uni-uni-, uni-bi-, and uni-trivalent salts;[1] and the decrease of the exponent with increasing concentration conforms also with that commonly shown by salts of lower valence types.[2] This shows that the principle that the form of the functional relation between ionization and concentration is the same whatever be the number of ions into which the salt dissociates is applicable even to these penta- and hexa-ionic salts of the uni-quadrivalent and uni-quinquivalent types.

In considering the effect of temperature on the ionization, it is best, owing to the considerable uncertainty in the μ_0 values obtained by extrapolation, to compare not the ratio $\mu\eta/\mu_0\eta_0$ (of which the values are given in Table VI), but the ratios $\mu\eta/\mu_{0\cdot2}\eta_{0\cdot2}$ (equal to $\gamma/\gamma_{0\cdot2}$) of the ionization at any higher concentration to that at 0.2 milliformal, since these do not involve the μ_0 values. The values of these ratios at the three temperatures for the concentrations 50 and 20 milliformal are as follows:

	Tetra-sodium salt.		Penta-sodium salt.	
	$\gamma_{50}/\gamma_{0\cdot2}$.	$\gamma_{20}/\gamma_{0\cdot2}$.	$\gamma_{50}/\gamma_{0\cdot2}$.	$\gamma_{20}/\gamma_{0\cdot2}$.
0°	53.1	60.2	47.0	53.7
25°	53.4	60.3	47.3	53.5
50°	52.8	59.5	46.3	51.7

It will be seen from the table that the change of the ionization with the temperature is so small as scarcely to exceed the possible experimental errors. There seeems, however, to be a slight decrease between 25° and 50° in the case of both salts.

12. Ionization in Relation to Valence Type.

One other salt of the uni-quadrivalent type, potassium ferrocyanide, has been accurately investigated.[3] It is therefore of interest to compare its ionization with that of the tetra-sodium salt considered in this article.

[1] Noyes and Johnston, THIS JOURNAL, 31, 1000 (1909).

[2] *Cf.* Abbott and Bray, *Ibid.*, 31, 746 (1909). This change in the exponent will be fully discussed in an article from this laboratory, soon to be published by Noyes and Faik.

[3] Conductance data for this salt were obtained by Noyes and Johnston (*loc. cit.*); viscosity data, by Wagner (*Z. physik. Chem.*, 5, 37 (1890)). The tetra- and penta-sodium salts of certain organic acids were measured by Ostwald (*Z. physik. Chem.*, 2, 903 (1888)) and by Walden (*Ibid.*, 8, 446 (1891)), but no special effort was made to derive an accurate conductance value at zero concentration.

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The ionization values at 25° (corrected for viscosity) of the two salts are as follows, those for the tetra-sodium salt having been derived from those in Table VI by graphical interpolation.

Formal conc.	$3^1/_8$.	$12^1/_2$.	25.	50.
K_4FeCN_6	71.2	59.0	53.6	49.6
$Na_4C_{11}H_2O_{10}$	70.1	57.9	52.8	48.2

It will be seen that these two very different salts have substantially the same ionization-values, thus confirming the principle that salts of the same valence type have in general approximately the same degree of ionization at the same concentration.

Another purpose of this investigation was to determine whether the principle that the fraction of a salt existing in the un-ionized state at any given molal concentration is roughly proportional to the product of the valences of its ions is applicable also to salts of high valence product, such as those involved in this research. This is shown to be the case by the following table, which gives the un-ionized fraction $(1-\gamma)$ at 25° when the salt is 0.05 formal, and the ratio of this fraction to the valence-product (v_1v_2), for these two salts (in the columns headed 4×1 and 5×1) and for the groups of salts of smaller valence-product considered in the article of Noyes and Johnston:

TABLE VII.—UN-IONIZED FRACTION IN RELATION TO VALENCE-PRODUCT.

v_2v_2.	1x1.	2x1.	3x1.	4x1.	5x1.	2x2.
$1-\gamma$	$0.13^1/_2$	0.28	0.39	0.52	0.60	0.58[1]
$(1-\gamma)/v_1v_2$	$0.13^1/_2$	0.14	0.13	0.13	0.12	$0.14^1/_2$

13. Summary.

In this article have been presented the results of measurements at 0°, 25°, and 50° of the formal (molal) conductance (μ), viscosity (η), and density of dilute solutions of the tetra-sodium and penta-sodium salts of benzenepentacarboxylic acid; also values of their conductance (μ_0) at zero concentration obtained by graphical extrapolation, and values (calculated from these data) of the ratio $\mu\eta/\mu_0\eta_0$, which expresses the ionization (γ) of the salts, if it be assumed that intermediate ions are not present.

The following principles, which had been previously derived from the study of salts of smaller valence-products, have been here shown to be applicable also to these two salts:

1. If the change of ionization with the concentration be expressed by a function of the form $C(1-\gamma) = K(C\gamma)^n$, it is found that the exponent n has approximately the same value (1.50 ± 0.05 at concentrations below 0.02 normal), whatever be the number of ions into which the salt dissociates, instead of a value equal to this number of ions, as would be required by the mass-action law. Moreover, as has been found with the salts of smaller valence-product, the value that has to be given

[1] This value is the average one for the sulfates of magnesium, zinc, and copper.

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to the exponent n is smaller at higher concentrations; thus it is 1.20 for these two salts for the concentration interval 0.01 to 0.1 normal.

2. The ionization of different salts of the same valence type is roughly the same at the same concentration. Thus that of the tetra-sodium salt has been shown to be substantially identical with that of potassium ferrocyanide, the other uni-quadrivalent salt that has been accurately investigated.

3. The un-ionized fraction of salts at a given formal (molal) concentration is roughly proportional to the product of the valences of their ions; thus at 0.05 formal the un-ionized fraction is $4 \times 13 = 52$ per cent. for the tetra-sodium salt, and $5 \times 12 = 60$ per cent. for the penta-sodium salt, while the average values previously obtained are $13^1/_2$ for uni-univalent, 2×14 for uni-bivalent, and 3×13 for uni-trivalent salts.

4. Increase of temperature causes only a slight decrease in the ionization of salts. Thus with these two salts the change between 0° and 25° is scarcely appreciable, and that between 25° and 50° amounts at 0.05 formal to 1.5 to 2 per cent. of the ionization value.

In addition, it is shown that at 25 and 50° the molal conductance of the quinquivalent ion $(C_{11}HO_{10})^V$ is 1.5 times that of the quadrivalent ion $C_{11}H_2O_{10}^{IV}$, while if these ions encountered the same frictional resistance the larger charge on the former ion would cause its molal conductance to be $5^2/4^2$ or 1.56 times that of the latter ion.

The conductance of benzenepentacarboxylic acid itself was also studied at 25° at the concentrations 0.0006 to 0.02 formal. The results show that it is a moderately strong acid with respect to both its first and second hydrogens.

BOSTON, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 70.]

THE PROPERTIES OF SALT SOLUTIONS IN RELATION TO THE IONIC THEORY. II. ELECTRICAL TRANSFERENCE NUMBERS.

BY A. A. NOYES AND K. G. FALK.

Received June 3, 1911.

CONTENTS.—Introduction. 6. Theoretical Considerations. 7. Review of Previous Investigations upon Transference Numbers. 8. Values of the Transference Numbers. 9. Comparison of Transference Numbers Derived by the Three Different Methods. 10. Change of the Transference Number with the Concentration and Temperature.

Introduction.

In a previous article[1] was presented the first part of a systematic critical study of the existing data relating to the properties of aqueous salt solutions, interpreted with reference to the Ionic Theory. This article de-

[1] THIS JOURNAL, 32, 1011–1030 (1910).

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scribes a continuation of that study. The work has been carried on with the aid of a grant from the Carnegie Institution of Washington, to which we desire to express our indebtedness.

6. Theoretical Considerations.

In the development of the Ionic Theory, as is well known, the mechanism of the conduction of electricity has played a most important part. The three factors upon which, in accordance with that theory, the rate at which electricity is transported through an electrolyte must depend are the number and nature of the ions present in it, the rates at which they move, and the electric charge carried by them.

There are three kinds of phenomena which are closely related to these factors. Of these phenomena may be first mentioned that which is quantitatively described by Faraday's Law, which in its general form may be stated as follows: The passage of electricity through an electrolyte is attended at each electrode by a chemical change involving a number of chemical equivalents strictly proportional to the quantity of electricity passed through and dependent on that alone. Faraday's Law, interpreted as a law of conduction, evidently signifies that motion of electricity in an electrolyte, takes place only in conjunction with motion of the ion-constituents,[1] and that equivalent quantities of different ion-constituents transport equal quantities of electricity.

The quantity of electricity producing a chemical change involving one equivalent is called one *faraday*, and is commonly represented by (F). Its value in the ordinary electrical units, taking the atomic weights of oxygen and silver as 16.00 and 107.88, according to the latest investigations[1] is 96,470 coulombs.[2] This quantity obviously represents the electrical charge on one equivalent weight of any ion.

A second electrical phenomenon that is of special importance in relation to the Ionic Theory is the conductance of solutions. This will be considered in the third paper of this series.

The third important phenomenon is that known as electrical transference, and to the consideration of this the present paper will be de-

[1] The term *ion-constituent* will be used in this series of articles to denote the positive or negative ion-forming constituent of the salt, without reference to the extent to which it may actually exist in the dissociated state. The term *ion* will be used to denote the electrically charged substances which have resulted from the dissociation of the salts and actually exist as such in the solution. The term *ion-molecules* will be used, when necessary, to denote the electrically charged particles, of which, according to the molecular theory, the ionic substances are composed; but when no confusion arises these ion-molecules may be called simply *ions*. Ion-constituents will be represented simply by the names and chemical formulas representing their composition (*e. g.*, sulfate, SO_4), ions by attaching to the name with a hyphen the word ion, and to the formula + or — signs representing the nature and magnitude of the electric charge (*e. g.*, sulfate-ion, $SO_4^{=}$).

[2] Smith, Mather, and Lowry, *Phil. Trans.*, 207, 579 (1908).

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voted. In these two papers, however, only the data relating to solutions of single salts will be discussed, mixtures being considered in later articles.

The phenomenon of transference is briefly described by the following statement: The passage of electricity through an electrolyte is attended by a partial transfer of the positive ion-constituents of the electrolyte from the neighborhood of the anode to that of the cathode, and of the negative ion-constituents from the neighborhood of the cathode to that of the anode; and the total number of equivalents of all the ion-constituents so transferred in both directions is equal to the number of faradays of electricity passed through.

The ordinary method of determining transference, which may be called the gravimetric method, consists in subjecting the quantities of the constituents found to be present after the electrolysis in a portion of the solution extending from the electrode to a distance from it beyond which no change in content has taken place, from the quantities of the same constituents known to be associated before the electrolysis with the weight of solvent present in that portion.

The ratio of the number of equivalents of any ion-constituent transferred to the cathode to the arithmetical sum of the total number of equivalents of all the ion-constituents transferred to and from the cathode is called the *transference number* (T) for that constituent. Thus if an electrolyte contains the basic or positive ion-constituents B', B'',...and the acidic or negative ion-constituents A', A'',...and the equivalents of these transferred to the cathode are $N_{B'}$, $N_{B''}$,..$N_{A'}$, $N_{A''}$,.. the transference number $T_{B'}$ of the constituent B', is:

$$T_{B'} = N_{B'}/(N_{B'} + N_{B''}..-N_{A'} - N_{A''}..) = N_{B'}/(\Sigma N_B - \Sigma N_A). \quad (10)$$

It is evident that the transference number of any ion-constituent is equal to the equivalents of it transferred when one faraday of electricity is passed through the electrolyte (since in that case $\Sigma N_B - \Sigma N_A = 1$).

It will be noted that the determination of transference by the gravimetric method is substantially equivalent to determining the relative quantities of the various ion-constituents which pass in either direction through a cross-section of the solution whose position is defined by the statement that the quantity of solvent between it and the electrode remains unchanged during the passage of the current. It is evident, therefore, that the quantity (N) of any ion-constituent transferred is equal to the product of (1) the area a of the cross-section, (2) the time t, (3) the velocity U with which the constituent moves through the imaginary cross-section, and (4) its equivalent concentration; that is, $N = a\,t\,U\,C$.[1]

[1] It is to be noted that N and U have negative values for negative ion-constituents under the convention here adopted, according to which transference and velocity, if taking place towards the cathode, are considered positive; if taking place away from the cathode, negative. The transference number T_A of a negative ion-constituent is therefore negative; and the relation $\Sigma T_B - \Sigma T_A = 1$ holds true.

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The transference number of an ion-constituent B' is therefore:

$$T_{B'} = U_{B'}C_{B'}/(U_{B'}C_{B'} + U_{B''}C_{B''}\ldots - U_{A'}C_{A'} - U_{A''}C_{A''}\ldots) = U_{B'}C_{B'}/(\Sigma U_B C_B - \Sigma U_A C_A). \quad (11)$$

In the case of a solution of a single salt, where there are only two ion-constituents (B and A) and where these have, necessarily, the same equivalent concentration, equation (11) assumes the simple form,

$$T_B = U_B/(U_B - U_A). \quad (12)$$

That is, the transference number of either ion-constituent is the ratio of its velocity to the arithmetical sum of the velocities of the two constituents.

This principle forms the basis of the moving-boundary method of determining transference numbers experimentally developed by Steele and Denison.[1] In this method the relative velocities, under the same conditions, of the two ion-constituents of a salt are obtained by measuring the distances traversed by the two boundaries of a solution of it placed between solutions of approximate concentration of two other salts, one of which has the same anion but a slower moving cation, and the other of which has the same cation but a slower moving anion, these conditions being essential to the maintenance of sharp boundaries. Thus the transference relations in a potassium chloride solution could be studied by placing it in a tube between solutions of sodium chloride and potassium acetate, passing a current in the direction from the sodium chloride to the potassium acetate, and measuring the distances traversed by the boundary between the sodium and potassium chloride and by that between the potassium chloride and acetate.

Since in carrying out this method the distances have always been measured with reference to a point outside of the solution, they must be corrected, as has been shown in detail by Lewis,[2] for any mass displacement of the liquid that may arise from volume changes attending the chemical processes taking place at the electrodes. If the apparatus is closed at the cathode side, the relation between the corrected and observed transference numbers is: $T^{corr} = T^{obs} + C\Delta v_c$, where C represents the equivalent concentration of the solution and Δv_c the volume-increase due to the changes taking place at the cathode when one faraday of electricity is passed. If it is closed at the anode side, the relation is $T^{corr} = T^{obs} - C\Delta v_A$, where Δv_A represents the volume-increase due to the changes taking place at the anode when one faraday is passed. (Unfortunately, in the experiments thus far published, the apparatus was

[1] Steele, *Z. physik. Chem.*, 40, 689 (1902). Denison, *Ibid.*, 44, 575 (1903). Denison and Steele, *Ibid.*, 57, 110 (1907). Denison, *Trans. Faraday Soc.*, 5, 165 (1909).

[2] THIS JOURNAL, 32, 863 (1910).

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left open at both sides, so that the correction to be applied is uncertain.[1]) It will be noticed that the correction is proportional to the concentration. At 0.1 normal it would hardly ever exceed a few tenths of a per cent., but at higher concentrations it is likely to be so large as to make the uncorrected results of little significance.

The transference numbers obtained by the moving-boundary method, when corrected for the mass displacement of the liquid, and those obtained by the gravimetric method are in principle identical quantities, as has been shown by Miller[2] and by Lewis.[3] Both methods give values that correspond to the relative quantities of the ion-constituent transferred measured with reference to an imaginary cross-section of the solution so placed that the same quantity of solvent is present on either side of it before and after electrolysis. They correspond, therefore, also to the relative velocities of the ion-constituents through the solvent (regarded as stationary).

Since the solvent may be itself transferred, owing to the ions of the salt being combined with it (*i. e.*, being solvated), the transference results obtained by either of these methods can be fully interpreted only up to moderate concentrations, up to which the solvation does not materially influence the results. At higher concentrations, however, there may be added to the solution some substance which presumably does not migrate with the current, and the transferred quantities not only of the ion-constituents but also of the solvent may be determined with reference to this substance. Experiments were first made in this way by Nernst, Gerrard, and Oppermann[4] by the gravimetric method; but only a few accurate results have been thus far published, namely, those obtained by Buchböck[5] with hydrochloric acid and by Washburn[6] with the alkali-element halides.

It is important, with reference to the theoretical significance of the results, to formulate the relation between the ordinary transference number T (referred to the solvent assumed stationary) and the "true" transference number T^{Tr} (referred to a non-migrating substance). This relation can readily be shown[7] to be

$$T^{Tr} = T + \Delta N_0 . N / N_0, \qquad (13)$$

[1] As suggested by Lewis, the best that can be done under these circumstances is to correct by means of the equation: $T^{corr} = T^{obs} + {}^1/_2(C\Delta v_C - \Delta v_A)$.

[2] *Z. physik. Chem.*, 69, 437 (1909).

[3] *Loc. cit.*

[4] *Nachrichten Göttinger Gesellsch. Wissensch.*, 56, 86 (1900).

[5] *Z. physik. Chem.*, 55, 563 (1906).

[6] THIS JOURNAL, 31, 349 (1909).

[7] Thus if the quantity of water ΔN_0 mols has come into the cathode portion through transference, the original content of that portion in any ion-constituent is obviously less than that ordinarily calculated, by the number of equivalents of the

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where ΔN_0 represents the number of mols of solvent transferred to the cathode per faraday and N the equivalents of salt in the solution associated with N_0 mols of the solvent.

The correction that must be added to the ordinary transference number to give the true transference number when N equivalents of the ion-constituent are associated with 1000 grams of water ($N_0 = 55.5$) is evidently $0.018\ N.\Delta N_0$. Thus for each mol of water transferred to the cathode per faraday it is 0.018 in a solution approximately normal, and 0.0018 in one approximatley 0.1 normal. The fractional correction is the ratio of this quantity to the transference number.

It is also to be noted that the solvent transferred to the cathode is the arithmetical difference between that carried to it by the positive ion-constituents and away from it by the negative ion-constituents. Thus, if in a solution of a single salt each equivalent of the positive constituent B carry n_W^B mols of water or other solvent and each equivalent of the negative constituent A carry n_W^A mols, and if the transference number of the former be T_B, then the solvent transferred per faraday would be

$$\Delta N_0 = n_W^B T_B + n_W^A T_A.^1 \qquad (14)$$

Attention may also be called to the fact that, if the ion-constituents of a salt are solvated, it is the true transference number, not the ordinary one, that must be substituted in equation (12) if U_B and U_A are to signify the velocities of the solvated ion-constituents through the (uncombined) solvent.

Next may be considered the factors which from a molecular standpoint must determin the velocity and transference of any ion-constituent, first in the case where it dissociates only into a single ion. Since at any moment only that fraction γ of the ion-constituent migrates which is in the state of (free) ion, the relation between the velocity (U_B or U_A) of the ion-constituent B or A and that (U_{B^+} or U_{A^-}) of the ion B^+ or A^- follows is:

$$U_B = \gamma_B U_{B^+}; \text{ or } U_A = \gamma_A U_{A^-}. \qquad (15)$$

In the case of a single salt consisting only of two such constituents, which must necessarily be equally dissociated ($\gamma_B = \gamma_A$), the degree of ionization will evidently not influence the transference number.

Any cause which affects differently the velocities of the two ions must, however, exert such an influence. Now the velocity of any (free) ion

ion-constituent associated in the solution with that quantity of water (that is, by $\Delta N_0 . N/N_0$). The number of equivalents of the constituent transferred to the cathode is therefore greater by the same amount.

[1] For example, assuming arbitrarily that the ions of sodium sulfate have the composition $(Na.2H_2O)^+$ and $(SO_4.8H_2O)^=$, equation (14) becomes (since $T_B = 0.39$ and $T_A = -0.61$) $\Delta N_0 = (2 \times 0.39) - (4 \times 0.61) = -1.66$ mols water per faraday. If the sodium ion be anhydrous, ΔN_0 would equal -2.44.

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must be equal to the ratio of the electric force driving it to the frictional resistance which it encounters when the velocity is unity.[1] The electric force under a given potential-gradient is proportional to the charge upon the ion and, therefore, to its valence. The frictional resistance may be expected to vary in the same direction in which the viscosity of the solution varies, the two variations being in general roughly proportional, but probably not exactly so, nor identically related in the case of different ions.[2] If the different ions are differently affected by changes in the medium, their relative velocities, and hence the transference number will evidently change with the concentration and temperature, though much less rapidly than the velocities of the separate ions. Since the viscosity of 0.1 normal solutions differs from that of water scarcely ever by more than 4 per cent., and usually by a much less amount, it is not to be expected that up to this concentration any considerable change in the transference number will take place from this cause; but it may well do so at considerably higher concentrations.

In the case in which there are two or more ions, $D'^{\pm}$ and $D''^{\pm}$ corresponding to an ion-constituent D (as would be true, for example, of either constituent of potassium sulfate if it be assumed that the salt is dissociated not only into K^+ and $SO_4^=$ ions, but also into KSO_4^- ions), the quantity of the constituent transferred is evidently equal to the algebraic sum of the two quantities of it that would be separately transferred as a result of the motions of the two ions containing it.[3] If the concentration of the constituent is C_D, the fraction of it existing as ion $D'^{\pm}$ is $\gamma_{D'}$, and that existing as ion $D''^{\pm}$ is $\gamma_{D''}$, and the velocities of these two are $U_{D'\pm}$ and $U_{D''\pm}$, then evidently the quantity of it passing through a cross-section of area a in the time t is $a\,t\,(\gamma_{D'}U_{D'\pm} + \gamma_{D''}U_{D''\pm})C_D$, and the resultant velocity U_D of the ion-constituent D is:

$$U_D = \gamma_{B'}U_{D'\pm} + \gamma_{D''}U_{D''\pm}. \qquad (16)$$

By substituting this value in equation (12) the following expression is obtained for a single salt whose two ion-constituents B and A are each transferred in the form of two or more ions:

$$\frac{T_B}{T_A} = \frac{\gamma_{B'}U_{B'\pm} + \gamma_{B''}U_{B''\pm} + \ldots}{\gamma_{A'}U_{A'\pm} + \gamma_{A''}U_{A''\pm} + \ldots}. \qquad (17)$$

Since the fractions $\gamma_{B'}$, $\gamma_{A'}$ . . of the ion-constituents dissociated into their various ions may change with the concentration, even while this is small,

[1] See Nernst, *Theoret. Chemie*, 4th edition, p. 13 (1903).

[2] For a fuller discussion of this relation, see the third paper of this series.

[3] That the presence of intermediate or complex ions has, as here postulated, no other effect on the concrete phenomena of transference than that of being one of the factors which determins the quantity of each ion-constituent transferred and its velocity through the solution has been shown by Lash Miller (*Z. physik. Chem.*, 69, 437 (1909).

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it is obvious that the transference number may do so likewise whenever intermediate or complex ions are present.

The application of this expression to the case in which a salt of the types B_2A or BA_2 (such as K_2SO_4 or $BaCl_2$) forms, in addition to the simple ions B^+ and A^-, an intermediate ion BA^- or BA^+ (such as KSO_4^- or $ClBa^+$) is of special importance. In this case expression (17) becomes

$$\frac{T_B}{T_A} = \frac{\gamma_B U_{B^+} + \gamma^B_{BA} U_{BA^\pm}}{\gamma_A U_{A^-} + \gamma^A_{BA} U_{BA^\pm}}, \qquad (18)$$

where γ^B_{BA} and γ^A_{BA} represent the fractions of the constituent A and of the constituent B, respectively, which exist in the form of the intermediate ion. Representing by γ_1 the fraction of the salt that is dissociated into BA^+ and BA^- or into A^- and BA^+, and by γ_2 the fraction of the salt that is dissociated into B^+ and A^-, the preceding equations may be written in the following forms:[1]

$$\frac{T_B}{T_A} = \frac{\left(\frac{\gamma_2}{\gamma_1} + \frac{1}{2}\right) U_{B^+} + \tfrac{1}{2} U_{BA^-}}{\frac{\gamma_2}{\gamma_1} U_{A^=} + U_{BA^-}} \text{ for a salt } B_2A. \qquad (19)$$

$$\frac{T_B}{T_A} = \frac{\frac{\gamma_2}{\gamma_1} U_{B^{++}} + U_{BA^+}}{\left(\frac{\gamma_2}{\gamma_1} + \frac{1}{2}\right) U_{A^+} + \tfrac{1}{2} U_{BA^+}} \text{ for a salt } BA_2. \qquad (20)$$

It is evident from these expressions that the transference number will, in general, vary with the ratio (γ_2/γ_1) of the fractions of the salt that are dissociated in the two ways. It can be shown, however, by differentiating these equations with respect to γ_2/γ_1 and placing the derivatives equal to zero, that the transference number will be independent of the character and extent of the ionization in the case that the following definit relation between the values of U_{B^+}, U_{A^-}, and U_{BA^-} holds true:

$$\frac{1}{U_{BA^-}} = \frac{2}{U_{A^=}} - \frac{1}{U_{B^+}} \text{ for } B_2A; \text{ or } \frac{1}{U_{BA^+}} = \frac{2}{U_{B^{++}}} - \frac{1}{U_{A^-}} \text{ for } BA_2. \qquad (21)$$

The separate terms in these expressions are evidently proportional to the frictional resistances which the ions encounter in their motion through the solution;[2] hence, it may be concluded that, in case the frictional resistance of the intermediate ion BA^- or BA^+ is the arithmetical sum

[1] These forms are obtained in the case of a salt B_2A by putting $\gamma_B = (\gamma_2 + \frac{1}{2}\gamma_1)$, $\gamma^B_{BA} = \frac{1}{2}\gamma_1$, $\gamma_A = \gamma_2$, and $\gamma^A_{BA} = \gamma_1$; and in the case of a salt BA_2 by putting $\gamma_B = \gamma_2$, $\gamma^B_{BA} = \gamma_1$, $\gamma_A = (\gamma_2 + \frac{1}{2}\gamma_1)$, and $\gamma^A_{BA} = \frac{1}{2}\gamma$; and by dividing both numerator and denominator by γ_1.

[2] This is true since the velocity is proportional to the ratio between the electric force driving the ion (which force is twice as great for a doubly as for a singly charged ion) and the frictional resistance which it encounters.

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of the frictional resistances of the simple ions B^+ and A^-, then the transference number will be independent of the proportion of intermediate ion that may be present.[1]

It is impossible to determin experimentally in any case whether the frictional resistance of the intermediate ion is really additive, since no method of obtaining the conductance or velocity of such ions in the case of salts has yet been developed. It may be pointed out, however, that such additivity implies, from the kinetic standpoint, the existence of a definit, unique relation between the dimensions of the single ions and that of the intermediate ion—a relation which, in view of the uncertainties as to the degree of proximity of the constituents in the intermediate ion and as to their relative hydration after union has taken place, can not be even approximately predicted. If, therefore, the transference number of any tri-ionic salt is found to be constant through a considerable range of concentration, this makes it somewhat probable, though it does not prove, that the intermediate ion is not present in considerable proportion in the solution. If such constancy of the transference number is found to be a common characteristic of tri-ionic salts, it shows that transference phenomena afford no evidence of the existence of intermediate ions.

Another special case in which a constituent may give rise to two or more different ions is that in which its ions may combine with different quantities of water. The relative proportions of the differently hydrated ions will, however, vary only when the solution becomes fairly concentrated. This matter will be more fully discussed in the third paper of this series.

Reference must finally be made to a third, somewhat indirect method which enables transference numbers and ionic velocities to be determined at zero concentration. This method is of especial importance since it is difficult to make accurate transference determinations at very small concentrations, since it affords a valuable check on the transference numbers directly obtained at greater concentrations, and since it enables new ones to be calculated. The method consists in determining first the equivalent conductances of the ions of some uni-univalent salt for which a reliable transference number at small concentrations has been measured, this being done by multiplying this transference number by the equivalent conductance of the salt at zero concentration. Then the conductances of other ions are derived by subtracting the known value for one of these ions from the equivalent conductance at zero concentration of other salts containing it. Since the equivalent conductance Λ_{B^+} or Λ_{A^-} is directly proportional to the velocity U_{B^+} or $-U_{A^-}$

[1] This conclusion has already been reached by Lewis, THIS JOURNAL, 32, 1569 (1910).

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under unit potential gradient, the transference numbers T_B and T_A are evidently given by the expressions:

$$T_B = \frac{\Lambda_{B+}}{\Lambda_{B+} + \Lambda_{A-}}; \text{ and } - T_{A-} = \frac{\Lambda_{A-}}{\Lambda_{B+} + \Lambda_{A-}}. \qquad (22)$$

The relation of equivalent conductance to ionic velocity and the possible errors involved in deriving by extrapolation the equivalent conductance of salts at zero concentration will be discussed more fully in the third paper. The values of the equivalent conductance of the salts and of the separate ions obtained from them as just described will also be there presented. The transference values calculated by means of equation (22) will, however, be included in this article, so that they may be compared with the results of direct determinations.

7. Review of Previous Investigations upon Transference Numbers.

In the following pages the attempt will first be made to bring together in tabular form all the fairly reliable transference values previously obtained for single salts in aqueous solution up to normal concentration, and to derive from these data the values which it seems best to adopt in the light of the now existing knowledge.[1] This section will be devoted to a consideration of the criteria of reliability in transference measurements and to a brief review of previously published investigations, especially with reference to the accuracy apparently secured and the relative weight that can appropriately be assigned to the results.

In determining the reliability of a transference determination by the gravimetric method the following factors are to be considered: 1. Whether the cathode and anode portions were both analyzed for one or both of the constituents, and how concordant the changes in content found in the two portions are. 2. The ratio of the change in content to the total content of the electrode portions, since, other things being equal, the accuracy increases as this ratio increases. 3. Whether one or more middle portions were analyzed, and the magnitnde of the change in content. 4. The character of the electrodes used, considered with reference to the possible formation of migrating substances and to the introduction of complications in the analysis of the electrode portions. 5. The character of the transference apparatus employed, especially with reference to the likelihood of convection during the electrolysis and during the subsequent removal of the portions, and with reference to the employment of membranes. 6. The probable accuracy of the analytical method employed. In addition, the usual criteria of a pre-

[1] A complete bibliography of articles relating to transference and a summary of all the transference data published up to the end of 1905 has been already published by McBain (*Proc. Washington Acad. Science*, 9, 1–78 (1907)). The present summary covers work published up to the end of 1910.

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cision discussion, such as the number of duplicate measurements made and the concordance of the results are also to be considered.

There are few physical or chemical measurements which yield results that afford so conclusive a test of their own accuracy as do complete transference measurements, by determining in both of the electrode portions the change in content of one, or still better, of both, of the constituents, and by making sure by the analysis of at least two middle portions that the change has not extended into them in consequence of convection or migration of products of the electrolysis. Comparatively few determinations, however, have been made in this complete way.

No results have been included in this article in which membranes were used in the transference apparatus, for Bein[1] and Hittorf[2] have shown that they frequently give rise to a selective transmission of the ions. Nor will any of the other results published prior to 1888 be included, as the errors involved in the early work were large for other reasons.

The investigations from which the results given in the next section of this article were taken may be briefly described as follows:

1. Löb and Nernst, *Z. physik. Chem.*, **2**, 948–958 (1888).

30 experiments on 10 silver salts at 0° and at 22–29° between 0.01 and 0.1 normal. Silver electrodes. Middle portion in a few of the experiments, but in these no change in content was found. Anode and cathode portions both analyzed. Analytical data not communicated except in a single experiment. Total amount of solution 40–60 cc., but percentage change in content very large. Weight assigned 1–2.

2. Bein, *Z. physik. Chem.*, **27**, 1–54 (1898).

154 experiments on most of the salts given in Table I at temperatures between 0° and 97°, mostly between 0.005 and 1.0 normal. Different forms of apparatus used, depending on concentration and temperature. Cathode, platinum; anode, cadmium or platinum (copper or silver in special cases). Total salt content unchanged. Middle portion in some experiments. Percentage change in content variable (10–20 per cent. in some experiments but amount of solution small). Weight assigned $^1/_2$–2, in general in accordance with the relative weights given by the author.

3. Hopfgartner, *Z. physik. Chem.*, **25**, 115–143 (1898).

65 experiments on sodium chloride, barium chloride, hydrochloric acid, copper sulfate, and magnesium sulfate at 6–26° between 0.1 and 1 normal. Cathode, mercury covered with concentrated zinc chloride solution; anode, copper for copper sulfate and magnesium sulfate, cadmium in other cases. One middle portion. Anode solution alone analyzed. Percentage change large. Weight assigned 2.

4. Mather, *Am. Chem. J.*, **26**, 473–491 (1901).

15 experiments on silver nitrate and silver acetate between 0° and 49.4° at 0.025 and 0.1 normal. No middle portion. Electrode solutions separated by a stopcock presumably of smaller cross section than remainder of apparatus. Silver electrodes. Both electrode solutions analyzed. Concentrations referred to definit volume of solution. Percentage change in content large. Weight assigned $^1/_2$.

5. Jahn and associates, *Z. physik. Chem.*, **37**, 673–712 (1901); **58**, 641–658 (1907).

[1] *Z. physik. Chem.*, **28**, 439 (1899).

[2] *Ibid.*, **39**, 613 (1902).

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Experimental work by students. Very large number of experiments on uni- and bivalent metal halides and sulfates, hydrochloric acid, nitric acid, and sulfuric acid, at 0°, 18° and 30° between 0.005 and 1 normal. One middle portion and anode solution only analyzed. Anode, zinc, cadmium or silver; cathode, mercury covered with a concentrated copper nitrate solution. Analytical work extremely accurate (details in first paper only). Percentage change in content large. Weight assigned 2.

6. Noyes, THIS JOURNAL, 23, 37–57 (1901).

20 experiments on potassium sulfate, barium chloride, and barium nitrate at 0.04 and 0.2 normal at 25°. Three middle and both electrode portions analyzed in case of barium nitrate, two middle portions and the cathode portion in case of the other salts. Platinum electrodes. Neutrality maintained by addition of requisit base or acid. Percentage change in content large. Weight assigned 6 in case of barium nitrate, 3 in other cases.

7. Noyes and Sammet, THIS JOURNAL, 24, 944–968 (1902); 25, 165–168 (1903).

42 experiments on hydrochloric acid at 10°, 20°, and 30° at 0.00556, 0.0167, and 0.051 normal. Both electrode portions and three middle portions analyzed. Silver anode; platinum cathode. Percentage change in content large. Weight assigned 6.

8. Steele and Denison, *J. Chem. Soc.*, 81, 456–469 (1902).

21 experiments on potassium chloride, and on calcium sulfate, nitrate, and chloride at 18° between 0.0025 and 0.0053 normal. One middle portion. Cathode portion only analyzed. Platinum electrodes. Neutrality maintained by addition of base and acid. Large volume of solution. Solution flowing through the two sides of apparatus. Percentage change in content large. Weight assigned 2.

9. Tower, THIS JOURNAL, 26, 1039–1065 (1904).

85 experiments on sulfuric acid at 8°, 20°, and 32° between 0.02 and 1 normal. Both electrode solutions and three middle portions analyzed. Cadmium anode; platinum cathode. Percentage change in content large. Weight assigned 4.

10. Jones and Bassett, *Am. Chem. J.*, 32, 429–438 (1904); Jones and Rouiller, *Ibid.*, 36, 462–466 (1906).

16 experiments on silver nitrate at 25° and 0°, at 0.1 and 0.02 normal. Silver electrodes. No middle portion. Both electrode portions analyzed. Separated by stopcock with bore 0.8 cm. diameter, remainder of apparatus 2 cm. diameter. Referred to constant volume. Percentage change in content large. Weight assigned $^1/_2$.

11. Noyes and Kato, THIS JOURNAL, 30, 318–334 (1908).

10 experiments on 0.0021 normal hydrochloric acid at 20° and 37 on nitric acid at 20° at 0.0022, 0.0067, 0.018, and 0.058 normal. Both electrode portions and three middle portions analyzed. Platinum electrodes. Percentage change in content large. Weight assigned 6 (at concentrations above 0.006 *N*).

12. Whetham and Paine, *Proc. Roy. Soc.*, 81A, 58–80 (1908).

4 experiments on sulfuric acid at 18° between 0.01 and 0.1 normal (also some with much more dilute solutions). Platinum electrodes. No middle portion. Concentration of electrode portions determined by conductance. Percentage change in content small. Weight assigned $^1/_2$.

13. Drucker and Krsnjavi, *Z. physik. Chem.*, 62, 731–742 (1908).

7 experiments on 0.0358 normal hydrochloric acid at 18° and 31°. Both electrode portions and three or five middle portions analyzed. Cathode, palladium; anode, palladium saturated with hydrogen. Percentage change in content large. Results from the two electrode portions not very concordant. Weight assigned 3.

14. Denham, *Z. physik. Chem.*, 65, 641–656 (1909).

4 experiments on cobalt bromide and cupric bromide at 25° between 0.17 and 0.92

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normal (also at higher concentrations). Cathode solution analyzed. No middle portion. Copper or cobalt anode; platinum cathode. Percentage change in content small. Weight assigned $^1/_2$.

15. Washburn, THIS JOURNAL, 31, 322–355 (1909).

3 experiments on sodium chloride, potassium chloride, and lithium chloride at 25° at 1.2–1.3 normal. Both electrode portions and three middle portions analyzed (for sodium chloride anode portion only). Reversible silver — silver chloride electrodes. Primarily a study of the relative hydration of the ions. Solutions contained also 0.1 mol raffinose per 1000 grams of water. Percentage change in content large. Weight assigned 3 for sodium chloride, 6 for the other two salts.

16. Riesenfeld and Reinhold, *Z. physik. Chem.*, 68, 440–458 (1909).

9 experiments on hydrochloric acid at 18–23° between 0.1 and 1.0 normal. Both electrode and two middle solutions analyzed. Nickel anode; platinum cathode. Percentage change in content large. Weight assigned 4.

17. Falk, THIS JOURNAL, 32, 1555–1571 (1910).

12 experiments on 0.03 and 0.1 normal thallous sulfate and lead nitrate at 25°. Both electrode portions and three middle portions analyzed. Thallium or lead anode; platinum cathode. Percentage change in content large. Weight assigned 4.

Comparatively few investigations have been described in which the moving-boundary method was employed. The results obtained by Lodge,[1] Whetham,[2] and Masson[3] are not accurate, because either gelatin was used or the composition of the solution was not definit, or for other reasons. In the earlier work of Steele,[4] gelatin was used to separate the electrode compartments from the tube in which the actual measurements of the speed of the boundary were made. This introduced considerable error owing to cataphoresis, as Abegg and Gaus[5] showed. Denison[6] studied, experimentally, the effect of the presence and absence of gelatin and of cataphoresis. He also measured a few transference values, but as these apply entirely to concentrations of 0.5 normal or greater, and as gelatin was used to separate the electrode compartments, they will not be used in this paper. The more recent work of Denison and Steele[7] and of Denison[8] was carried on without the use of gelatin or of any membrane; but no correction was made for changes in the volume resulting from the reactions taking place at the electrodes.[9] For this reason only the results will be used that were obtained at concentrations not greater than 0.1 normal, up to which the volume correction is not important.

8. Values of the Transference Numbers.

Table IV contains the values of the cation-transference numbers ($\times 10^3$)

[1] *British Assoc. Rep.*, 389 (1886).
[2] *Phil. Trans.*, 184A, 337 (1893); 186A, 507 (1895).
[3] *Z. physik. Chem.*, 29, 501 (1899).
[4] *Phil. Trans.*, 198A, 105; *Z. physik. Chem.*, 40, 689 (1902).
[5] *Z. physik. Chem.*, 40, 737 (1902).
[6] *Ibid.*, 44, 575 (1903).
[7] *Phil. Trans.*, 205A, 449; *Z. physik. Chem.*, 57, 110 (1906).
[8] *Trans. Faraday Soc.*, 5, 164 (1909).
[9] Cf. Lewis, THIS JOURNAL, 32, 862 (1910).

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TABLE IV.—VALUES OF THE CATION-TRANSFERENCE NUMBER × 10^3 OBTAINED BY THE GRAVIMETRIC METHOD.

Substance.	Temp.	Observer.	Wt.	0.002 to 0.008	0.008 to 0.015	0.015 to 0.025	0.025 to 0.040	0.04 to 0.06	0.06 to 0.08	0.08 to 0.15	0.15 to 0.25	0.25 to 0.40	0.40 to 0.60	0.60 to 0.80	0.8 to 1.0
NaCl	0	Jahn, Schulz	2	388	388	387	387	...	386	385	...	...	...	...	...
	7.5	Bein	1	...	...	...	...	...	...	...	...	383	...	...	...
	10.5	Bein	1	382	394	...	...	...	386	...	...	...	...	...	...
	16	Hopfgartner	2	...	...	...	...	...	...	383	378	...	377	365	365
	18	Jahn, Schulz, Bogdan	2	...	396	397	395	...	395	395	...	...	...	...	...
	19	Bein	1	...	...	...	...	392	...	...	...	...	...	...	...
	25	Washburn	3	...	...	...	...	...	...	...	...	...	...	...	366*
	30	Jahn, Schulz	2	405	405	404	403	...	404	403	...	...	...	...	...
	51	Bein	1	...	418	...	...	...	...	...	...	...	...	...	...
	76	Bein	1	...	...	...	...	...	414	430	...	...	...	...	...
	96	Bein	1	...	453	...	...	441	...	...	...	443	...	...	...
KCl	0	Jahn, Hertz	2	495	494	493	491	491	...	491	491	...	...	...	...
	10	Bein	2	...	495	...	...	...	...	495	...	...	...	...	...
	18	Steele, Denison	2	495	...	...	...	...	...	...	...	...	...	...	...
	18	Jahn, Bogdan, Hertz	2	...	498	498	495	493	...	495	494	...	...	...	...
	25	Washburn	6	...	...	...	...	...	...	...	...	...	...	...	482*
	30	Jahn, Hertz	2	498	499	499	499	497	...	498	496	...	...	...	...
	76	Bein	½	...	...	...	...	...	...	490	482	...	...	...	...
LiCl	10	Bein	½	...	...	...	...	...	...	339	...	...	...	...	...
	18	Jahn, Goldhaber	2	...	330	330	330	...	316	312	...	300	...	...	...
	18	Bein	½	...	...	...	...	...	333	...	...	...	...	...	...
	20.5	Bein	2	...	376	...	...	...	...	...	...	...	...	...	...
	24	Bein	2	...	...	...	...	324	...	...	...	...	...	...	...
	25	Washburn	6	...	...	...	...	...	...	...	...	...	...	...	276*
	97	Bein	1	...	379	...	...	390	...	...	...	...	...	...	...
NH_4Cl	0	Jahn, Schulz, Hertz	2	...	490	489	487	...	...	...	...	...	...	...	...
	18	Jahn, Schulz, Hertz	2	...	493	491	490	...	...	...	...	...	...	...	...
	20	Bein	2	...	...	...	...	493	...	...	...	...	...	...	...
	30	Jahn, Schulz, Hertz	2	...	496	495	494	...	...	...	...	...	...	...	...
NaBr	18	Jahn, Bogdan, Oppenheimer	2	394	395	396	393	...	...	...	...	...	...	...	...

* Concentration = 1.25 normal.

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TABLE IV.—VALUES OF THE CATION-TRANSFERENCE NUMBER × 10^3 OBTAINED BY THE GRAVIMETRIC METHOD (*Continued.*)

Substance.	Temp.	Observer.	Wt.	0.002 to 0.008	0.008 to 0.015	0.015 to 0.025	0.025 to 0.040	0.04 to 0.06	0.06 to 0.08	0.08 to 0.15	0.15 to 0.25	0.25 to 0.40	0.40 to 0.60	0.60 to 0.80	0.8 to 1.0
NaBr	22	Bein	1	...	...	...	...	375	...	...	...	...	...	...	...
KBr	18	Jahn, Hertz, Bogdan	2	...	495	496	495	...	...	...	...	...	...	...	...
$AgNO_3$	0	Jones, Bassett, Rouiller	½	...	...	445	...	...	...	437	...	...	...	...	...
	0	Löb, Nernst	2	...	...	462	...	...	...	...	...	...	...	...	...
	0	Mather	½	...	...	462	...	...	...	459	...	...	...	...	...
	18	Jahn, Berliner	2	474	469	472	472	...	...	...	...	...	...	...	...
	20	Löb, Nernst	2	...	...	...	...	...	...	472	...	...	...	...	...
	25	Jones, Bassett, Rouiller	½	...	...	460	...	...	...	472	...	...	...	...	...
	26	Löb, Nernst	2	...	478	478	...	476	...	...	...	...	...	...	...
	29.1	Mather	½	...	...	...	...	...	...	468	...	...	...	...	...
	30	Jahn, Berliner	2	482	481	482	482	...	475	480	485	...	481	...	...
	46.5	Mather	½	...	...	475	...	...	...	472	...	...	...	...	...
	74	Bein	½	...	...	...	...	483	...	...	...	...	...	...	...
$AgC_2H_3O_2$	0	Mather	½	...	...	627	...	...	...	...	...	...	...	...	...
	24	Bein	1	...	...	...	...	587	...	...	...	...	...	...	...
	24.5	Löb, Nernst	2	...	624	...	...	...	...	...	...	...	...	...	...
	28.3	Mather	½	...	...	618	...	...	...	...	...	...	...	...	...
	46.5	Mather	½	...	...	611	...	...	...	...	...	...	...	...	...
	96	Bein	½	...	...	...	562	...	...	...	...	...	...	...	...
HCl	0	Jahn, Joachim, Wolff	2	847	847	845	840	...	839	833	...	...	...	...	...
	9.5	Bein	1	832	834	...	...	...	...	...	...	...	...	...	...
	10	Noyes, Sammet	6	...	...	841	...	...	...	...	...	...	...	...	...
	14	Bein	2	...	...	...	...	...	...	830	...	...	...	...	...
	18	Jahn, Joachim, Wolff	2	833	833	833	835	...	...	...	...	...	...	...	...
	18	Drucker, Krsnjavi	3	...	...	...	833	...	...	...	...	...	...	...	...
	18	Bein	1	...	...	...	...	834	...	...	...	...	...	...	...
	18	Hopfgartner	2	...	...	...	...	...	...	833	836	...	833	843	841
	18	Riesenfeld, Reinhold	4	...	...	...	...	...	...	839	...	...	844	...	845
	20	Noyes, Sammet	6	833[1]	...	833	...	834	...	...	...	...	...	...	...

[1] At 0.00556 normal.

HCl	*20*	*Noyes, Kato*	2	829[1]	...	...	...	...	...	...	...	...	...	...	...

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HCl	20	*Noyes, Kato*	2	829[1]	...	...	...	...	...	...	...	...	...	...
	30	*Jahn, Joachim, Wolff*	2	817	817	818	819	...	820	814	...	...	...	...
	30	*Noyes, Sammet*	6	...	...	823	...	...	...	...	...	...	...	...
	31	*Drucker, Krsnjavi*	3	...	...	...	821	...	...	...	...	...	...	...
	50	Bein	2	...	801	...	...	...	...	...	...	...	...	...
	76.5	Bein	1	...	...	...	...	...	781	781	...	...	...	...
	96.5	Bein	2	...	748	...	...	...	...	...	...	...	...	...
HNO_3	18	Jahn, Bukschnewski	2	829	830	830	829	...	830	832	830	...	...	...
	20	Noyes, Kato	6	839[2]	...	840	...	844	...	...	...	...	...	...
	25	Bein	½	...	...	...	...	828	...	...	...	...	...	...
$BaCl_2$	0	Jahn, Wolff	2	438	438	434	427	...	...	...	...	...	...	...
	11	Bein	2	...	441	...	...	...	...	429	417	416	...	...
	16	Hopfgartner	2	...	...	...	...	...	...	421	408	...	389	383
	18	Jahn, Bukschnewski	2	447	447	452	457	...	...	...	...	...	...	...
	25	Noyes	3	...	...	...	442	...	...	...	415	...	...	...
	30	Jahn, Wolff	2	445	445	443	443	...	...	...	...	...	...	...
	50	Bein	1	...	475	...	...	...	...	...	...	...	...	...
	76	Bein	½	...	...	...	...	...	...	447	...	...	...	...
	97	Bein	½	...	485	...	...	...	...	...	446	...	...	...
$CaCl_2$	18	Steele, Denison	2	438	...	...	...	...	...	...	...	...	...	...
	21	Bein	1	...	447	...	...	...	...	...	395	390	...	...
	24.5	Bein	2	...	...	...	...	418	...	405	...	...	...	...
	49	Bein	1	...	445	...	...	...	...	...	...	...	...	...
	96	Bein	1	...	470	...	...	...	...	426	451	...	...	...
$SrCl_2$	20.5	Bein	1	...	440	...	...	425	...	...	...	...	...	...
$CdCl_2$	8	Bein	1	...	...	...	...	...	...	...	...	433	...	...
	17	Bein	½	...	...	...	...	...	...	433	...	...	...	...
	18	Jahn, *et al.*[3]	2	430	431	429	431	429	432	430	...	...	...	...
	20	Bein	1	...	443	...	...	...	...	...	...	...	...	...

[1] At 0.0021 normal.

[2] 837 at 0.0022 normal, and 840 at 0.0067 normal.

[3] Jahn, Goldhaber, and Bukschnewski.

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TABLE IV.—VALUES OF THE CATION-TRANSFERENCE NUMBER × 10^3 OBTAINED BY THE GRAVIMETRIC METHOD (*Continued*).

Substance.	Temp.	Observer.	Wt.	0.002 to 0.008	0.008 to 0.015	0.015 to 0.025	0.025 to 0.040	0.04 to 0.06	0.06 to 0.08	0.08 to 0.15	0.15 to 0.25	0.25 to 0.40	0.40 to 0.60	0.60 to 0.80	0.8 to 1.0
$CdCl_2$	24.5	Bein	1	...	...	...	...	431	...	...	...	...	...	...	...
	96	Bein	1	...	...	...	...	525	...	...	...	...	...	...	...
$CdBr_2$	18	Jahn, *et al.*[1]	2	426	428	430	431	431	434	432	423	399	350	...	218
CdI_2	18	Jahn, *et al.*[2]	2	444	442	443	425	407	381[3]	...[3]	...[3]	...[3]	...[3]	...	...
Na_2SO_4	18	Jahn, Goldlust	2	...	392	391	387	...	379	...	...	...	...	...	...
K_2SO_4	18	Jahn, Goldlust	2	...	494	495	490	...	488	...	...	...	...	...	...
	25	Noyes	3	...	...	...	496	...	...	...	493	...	...	...	...
Tl_2SO_4	23	Bein	1	...	...	...	...	472	...	...	...	...	...	...	...
	25	Falk	4	...	...	...	479	...	...	476	...	...	...	...	...
H_2SO_4	8	Tower	4	...	...	832	...	836	...	836	...	...	...	...	...
	11	Bein	2	...	...	...	...	825	...	...	...	...	...	...	...
	18	Whetham, Paine	½	...	814	...	...	...	...	814	...	...	...	...	...
	18	Jahn, Hugbrechts	2	...[4]	...[4]	824	825	...	826	824	832	...	...	...	...
	20	Tower	4	...	...	819	...	821	...	824	819	...	813	...	812
	30	Jahn, Hugbrechts	2	...[5]	...[5]	814	812	...	805	...	...	...	...	...	...
	32	Tower	4	...	...	809	...	808	...	808	...	...	...	...	...
	96	Bein	1	...	...	...	...	696	...	...	...	...	...	...	...
$Ba(NO_3)_2$	25	Noyes	6	...	...	...	456	...	...	...	455	...	...	...	...
$Pb(NO_3)_2$	25	Falk	4	...	...	...	487	...	...	487	...	...	...	...	...
$MgSO_4$	12	Hopfgartner	2	...	...	...	...	...	...	...	...	...	...	...	25.
	18	Jahn, Hugbrechts	2	387	386	381	376	...	369	...	...	...	...	...	...
	24	Bein	1	...	...	...	...	459	...	...	...	...	...	...	...
	30	Jahn, Hugbrechts	2	...	388	387	384	...	376	...	...	...	...	...	...
$CdSO_4$	18	Jahn, Goldlust, Redlich	2	...	388	386	381	379	371	365	354	341	323	...	294
$CuSO_4$	0	Bein	1	...	385	...	...	...	...	389	...	...	...	...	...
	11	Hopfgartner	2	...	...	...	...	...	...	...	...	...	...	316	304
	15	Bein	1	...	367	...	...	...	...	...	368	...	...	...	...
	18	Jahn, Metelka	2	...	...	375	375	375	376	374	366	328	328	...	...
	50	Bein	1	...	...	...	...	...	...	393	...	...	...	...	...
	76	Bein	½	...	...	...	...	...	...	...	378	...	...	...	...

[1] John, Goldhaber, and Bukschnewski.
[2] Jahn, Redlich, and Bukschnewski.
[3] 343 at 0.08 normal, 281 at 0.12 normal, 223 at 0.16 normal, 75 at 0.25 normal, and —3 at 0.5 normal.
[4] 824 at 0.011 normal, 827 at 0.010 normal, 843 at 0.0093 normal, and 845 at 0.0078 normal.
[5] 816 at 0.012 normal, 830 at 0.0097 normal, 839 at 0.0093 normal, and 838 at 0.0081 normal.

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Substance.	Temp.	Observer.	Wt.	0.002–0.008	0.008–0.015	0.015–0.025	0.025–0.040	0.04–0.06	0.06–0.08	0.08–0.15	0.15–0.25	0.8–1.0
RbCl	22	Bein	1	...	...	...	...	485	...	...	...	...
CsCl	20	"	1	...	...	...	...	492	...	...	...	...
TlCl	22	"	1	...	484	...	...	...	...	...	...	...
KI	25	"	1	...	...	...	...	495	...	...	...	...
NaOH	25	"	1/2	...	...	...	201	...	...	...	...	...
$NaNO_3$	19	"	1	...	...	...	...	371	...	...	...	...
$KMnO_4$	23	"	1	...	...	...	...	441	...	...	...	...
$AgClO_3$	25	Löb, Nernst	1	...	...	499	...	...	...	...	...	...
$AgClO_4$	25	"	1	...	...	486	...	...	...	...	...	...
$AgC_2H_5SO_4$	25	"	2	616	...	613	...	...	...	...	...	...
$AgSO_3C_{10}H_7$	25	"	1	...	...	614	...	...	...	...	...	...
	29	"	1	...	610	...	...	...	...	...	...	...
$AgSO_3C_6H_5$	25	"	1	...	...	653	...	...	...	...	...	...
$AgSO_3C_9H_{11}$[1]	0	"	1	...	...	727	...	...	...	...	...	...
	24	"	1	...	...	707	...	...	...	...	...	...
	29	"	1	...	...	705	...	...	...	...	...	...
$Ag_2S_2O_6$	0	"	1	...	...	396	...	...	...	...	...	...
	24.5	"	1	...	...	395	...	...	...	...	...	...
	29	"	1	...	...	396	...	...	...	...	...	...
Ag_2SiF_6	22	"	1	...	...	...	535	...	...	...	...	...
$MgCl_2$	21	Bein	1	...	...	...	...	385	...	...	...	...
$MnCl_2$	18	"	1	...	...	...	...	387	...	...	...	...
$CuCl_2$	23	"	1	...	...	...	...	405	...	...	...	...
$CoCl_2$	18	"	1	...	...	...	...	404	...	...	...	...
$CoBr_2$	25	Denham	1	...	...	...	...	...	...	...	409	413
$CuBr_2$	25	"	1	...	...	...	...	...	...	...	445	440
$Ca(OH)_2$	24.5	Bein	1	...	...	...	214	...	...	...	...	...
$Ca(NO_3)_2$	18	Steele, Denison	2	450	...	...	...	...	...	...	...	...
$CaSO_4$	18	"	2	441	...	...	...	...	...	...	...	...

obtained by the gravimetric method by various investigators. The headings of the first four columns are self-explanatory; those of the following columns show the content of solution expressed in equivalents of substance per liter of solution. For convenience in tabulation all the results obtained at any content falling within the small intervals indicated by the headings have been placed in the same column. The weights assigned are only estimates based upon the considerations presented in the last section, without reference to the agreement of the results with those of other investigators.

In order to determin the best values to adopt for the transference numbers, the method of procedure was as follows: In cases in which the transference number shows throughout a considerable concentration-interval a change not greater than corresponds to the probable experimental error, the weighted mean of all the values within such an interval

[1] Silver pseudocumenesulfonate.

[2] 343 at 0.08 normal, 281 at 0.12 normal, 223 at 0.16 normal, 75 at 0.25 normal, and —3 at 0.5 normal.

[3] 824 at 0.011 normal, 827 at 0.010 normal, 843 at 0.0093 normal, and 845 at 0.0078 normal.

[4] 816 at 0.012 normal, 830 at 0.0097 normal, 839 at 0.0092 normal, and 838 at 0.0081 normal.

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was taken. In cases in which there was an appreciable change with the concentration, the transference numbers were plotted against the logarithm of the concentration, and the curve was drawn best representative of the separate results, regard being paid to their relative weights. (When results exist at different temperatures removed from each other by only two or three degrees, they were first reduced to a common temperature.)

Table V contains the values so derived. Isolated results of small weight and a few sets of values which are obviously inaccurate are omitted. The scattering results for the 24 salts grouped together at the end of Table IV are also not reproduced in Table V, in order to avoid unnecessary repetition.

The weights assigned refer, in general, to the values given for concentrations between 0.01 and 0.1 normal. They are based on the number and concordance of the separate data involved and on the weights assigned to them in Table IV.

TABLE V.—BEST VALUES OF THE CATION-TRANSFERENCE-NUMBER $\times 10^3$.

Substance.	Temp.	Wt.	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.5	1.0
NaCl	0	2	387	387	387	386	385	...	...	...	...
	18	4	396	396	396	395	393	390	388	382	369
	30	2	404	404	404	404	403	...	...	...	...
	96	1	...	...	...	442	442	442	...	...	...
KCl	0	2	493	493	493	493	492	491	...	...	...
	10	1	...	495	495	495	495	...	...	...	...
	18	3	496	496	496	496	495	494	...	...	...
	30	2	498	498	498	498	497	496	...	...	...
LiCl	18	2	...	332	328	320	313	304	299	...	...
NH_4Cl	0	2	...	489	489	...	...	...	...	...	...
	18	3	...	492	492	492	...	...	...	...	...
	30	2	...	495	495	...	...	...	...	...	...
NaBr	18	2	395	395	395	...	...	...	...	...	...
KBr	18	2	...	495	495	...	...	...	...	...	...
$AgNO_3$	0	2	...	...	461	...	...	...	...	...	...
	18	2	...	471	471	471	471	...	...	...	...
	25	2	...	477	477	477	...	...	...	...	...
	30	2	481	481	481	481	481	481	481	481	...
HCl	0	1	847	846	844	839	834	...	...	...	...
	10	6	840	840	841	...	...	...	...	...	...
	18	15	832	833	833	834	835	837	838	840	844
	30	9	...	822	822	822	...	...	...	...	...
	50	2	...	801	...	...	...	...	...	...	...
	76	2	...	...	...	...	781	...	...	...	...
	96	2	...	748	...	...	...	...	...	...	...
HNO_3	20	6	839	840	841	844	...	...	...	...	...
$BaCl_2$	0	2	439	437	432	...	...	...	...	...	...
	11	2	...	441	...	...	...	...	...	...	...
	16	2	...	...	...	...	420	408	401	391	...
	25	3	...	...	...	438	427	415	...	...	...
	30	2	445	444	443	...	...	...	...	...	...
	50	1	...	475	...	...	...	...	...	...	...

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TABLE V (*continued*).

Substance.	Temp.	Wt.	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.5	1.0
$CaCl_2$	20	2	440	432	424	413	404	395	389	...	...
	25	2	...	...	...	418	409	...	...	...	...
$SrCl_2$	20	1	...	441	435	427	...	...	...	...	...
$CdCl_2$	18	2	430	430	430	430	430	...	...	...	...
$CdBr_2$	18	2	430	430	430	430	429	410	389	350	222
CdI_2	18	2	445	444	442	396	296	127	46	3	...
Na_2SO_4	18	2	...	392	390	383	...	...	...	...	...
K_2SO_4	18	2	...	494	492	490	...	...	...	...	...
	25	3	...	...	...	496	494	493	...	...	...
Tl_2SO_4	25	4	...	...	...	478	476	...	...	...	...
H_2SO_4	8	4	...	...	835	835	835	...	...	...	...
	20	6	...	...	822	822	822	820	818	816	812
	32	5	...	...	808	808	808	...	...	...	...
$Ba(NO_3)_2$	25	6	...	...	...	456	456	456	...	...	...
$Pb(NO_3)_2$	25	4	...	...	...	487	487	...	...	...	...
$MgSO_4$	18	2	388	385	381	373	...	...	...	...	...
	30	2	...	388	386	380	...	...	...	...	...
$CdSO_4$	18	2	...	389	384	374	364	350	340	323	294
$CuSO_4$	18	2	...	...	375	375	373	361	348	327	...

Table VI contains the results obtained by Denison and Steele and by Denison by the moving-boundary method. The concentrations are given in equivalents of substance per liter of solution.

TABLE VI.—VALUES OF THE CATION-TRANSFERENCE-NUMBER × 10^3 OBTAINED BY THE MOVING-BOUNDARY METHOD.

Substance.	18° 0.02	18° 0.05	18° 0.1	25° 0.1	Substance	18° 0.02	18° 0.05	18° 0.1	25° 0.1
NaCl	...	387	383	...	K_2SO_4	488	...	485	479
KCl	493	...	492	493	H_2SO_4	833	...	828	...
RbCl	497	...	494	...	$BaCl_2$	435	...	419	416
CsCl	504	...	500	...	$CaCl_2$	413	...	398	396
NH_4Cl	492	...	489	...	$SrCl_2$	412	...	400	404
NaBr	...	381	376	...	$MgCl_2$	...	368	352	...
KBr	482	...	481	480	$BaBr_2$	422	...	408	...
RbBr	495	...	492	...	$CaBr_2$	409	...	396	...
CsBr	497	...	493	...	$SrBr_2$	410	...	392	...
NH_4Br	483	...	481	...	$MgBr_2$	385	368	350	...
NaI	...	381	376	...	BaI_2	426	...	415	...
KI	487	...	486	483	CaI_2	416	...	400	...
RbI	498	...	497	...	SrI_2	416	...	393	...
CsI	497	...	497	...	MgI_2	388	...	350	...
NH_4I	489	...	484	...	....	...	...	...	...
KNO_3	502	...	502	501	....	...	...	...	...
$KClO_3$	534	...	536	537	....	...	...	...	...
$KBrO_3$	567	...	570	570	....	...	...	...	...
$KClO_4$	...	...	523	...	....	...	...	...	...
NaOH	...	...	158	...	....	...	...	...	...
KOH	...	...	257	...	....	...	...	...	...
HCl	835	...	835	...	....	...	...	...	...
HNO_3	846	...	855	...	....	...	...	...	...

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9. Comparison of Transference Numbers Derived by the Three Different Methods

Before discussing the general significance of the results, it seems desirable to show the degree of concordance of the transference numbers obtained by the three independent methods—the gravimetric method, the moving-boundary method, and the conductance method. The well-known principles involved in these methods have been discussed in Section 6.

In Table VII are placed side by side the values obtained by these three methods at 18° and 25° at various equivalent concentrations up to 0.2 normal. The results by the conductance method are those given under the concentration-heading 0.0. They were calculated by equation (22) of Section 6 from the values of the equivalent conductances of the separate ions, which will be tabulated in the third paper of this

TABLE VII.—COMPARISON OF TRANSFERENCE NUMBERS DERIVED BY THE DIFFERENT METHODS.

VALUES AT 18°.

Substance.	0.0		0.005	0.02	0.05	0.10	0.20
NaCl	399	Gr(4)	396	396	395	393	390
		MB	...	...	386	383	...
KCl	496	Gr(3)	496	496	496	495	494
		MB	...	493	...	492	...
LiCl	337	Gr(2)	...	328	320	313	304
NH_4Cl	497	Gr(3)	...	492	492	...	...
		MB	...	492	...	489	...
RbCl	508	MB	...	497	...	494	...
CsCl	509	MB	...	504	...	500	...
NaBr	391	Gr(2)	395	395	...	...	...
		MB	...	...	381	376	...
KBr	488	Gr(2)	...	495	...	...	...
		MB	...	482	...	481	...
RbBr	499	MB	...	495	...	492	...
CsBr	501	MB	...	497	...	493	...
NH_4Br	489	MB	...	483	...	481	...
NaI	395	MB	...	...	381	376	...
KI	492	MB	...	487	...	486	...
RbI	503	MB	...	498	...	497	...
CsI	505	MB	...	497	...	497	...
NH_4I	493	MB	...	489	...	484	...
KNO_3	511	MB	...	502	...	502	...
$AgNO_3$	466	Gr(2)	...	471	471	471	...
$KClO_3$	539	MB	...	534	...	536	...
$KBrO_3$	575	MB	...	567	...	570	...
HCl	828	Gr(15)	832	833	834	835	837
		MB	...	835	...	835	...
HNO_3	836	Gr(6)	839	841	844	...	...
		MB	...	846	...	855	...

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TABLE VII (*Continued*).

VALUES AT 18°.

Substance.	0.0		0.005	0.02	0.05	0.10	0.20
$BaCl_2$	458	Gr(2)	...	...	...	422	410
		MB	...	435	...	419	...
$CaCl_2$	442	Gr(2)	438	422	411	402	393
		MB	...	413	...	398	...
$SrCl_2$	442	Gr(2)	...	433	425	...	...
		MB	...	412	...	400	...
$MgCl_2$	412	MB	...	...	368	352	...
$BaBr_2$	450	MB	...	422	...	408	...
$CaBr_2$	434	MB	...	409	...	396	...
$SrBr_2$	434	MB	...	410	...	392	...
$MgBr_2$	404	MB	...	385	368	350	...
BaI_2	454	MB	...	426	...	415	...
CaI_2	438	MB	...	416	...	400	...
SrI_2	438	MB	...	416	...	393	...
MgI_2	408	MB	...	388	...	350	...
Na_2SO_4	388	Gr(2)	...	390	383	...	...
K_2SO_4	485	Gr(2)	...	492	490	...	...
		MB	...	488	...	485	...
H_2SO_4	821	Gr(6)	...	824	824	824	822
		MB	...	833	...	828	...
$Ca(NO_3)_2$	456	Gr(2)	450	...	...	...	...
$MgSO_4$	401	Gr(2)	388	381	373	...	...
$CdSO_4$	404	Gr(2)	...	384	374	364	350
$CuSO_4$	401	Gr(2)	...	375	375	373	361
$CaSO_4$	431	Gr(2)	441	...	...	...	...

VALUES AT 25°.

NaCl	403	Gr(3)	400	400	399	397	394
KCl	497	Gr(3)	497	497	497	496	495
		MB	...	...	...	493	...
NH_4Cl	497	Gr(3)	...	494	494	...	...
KI	494	MB	...	...	...	483	...
$AgNO_3$	473	Gr(2)	...	477	477	...	...
KNO_3	514	MB	...	...	...	501	...
HCl	822	Gr(12)	...	826	826	827	...
$KBrO_3$	577	MB	...	...	...	570	...
$BaCl_2$	462	Gr(3)	...	...	438	427	415
		MB	...	...	...	416	...
$CaCl_2$	442	Gr(2)	...	...	418	409	...
		MB	...	...	...	396	...
K_2SO_4	483	Gr(3)	...	...	496	494	493
		MB	...	...	...	479	...
Tl_2SO_4	487	Gr(4)	...	479[1]	478	476	...
H_2SO_4	814	Gr(6)	...	817	817	817	...
$Ba(NO_3)_2$	480	Gr(6)	...	...	456	456	456
$Pb(NO_3)_2$	502	Gr(4)	...	487[1]	487	487	...
$MgSO_4$	407	Gr(1)	...	384	377	...	...

[1] At 0.03 normal.

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series.[1] The results by the gravimetric method are preceded by the letters Gr; those by the moving-boundary method by the letters MB. The figures within parentheses following the letters Gr show the weights attributed to the results at the concentrations 0.02 to 0.1 normal.

An examination of Table VII shows that the values at 18° obtained by the gravimetric and moving-boundary methods are concordant within about 1 per cent. for hydrochloric, nitric and sulfuric acids, potassium chloride, ammonium chloride, and potassium sulfate, but that those by the gravimetric method are considerably larger (usually by 2.5 to 3.0 per cent.) for the other six substances that have been investigated by both methods. The values obtained by the conductance method with uni-univalent salts are also almost uniformly 1 to 3 per cent. higher than those by the moving-boundary method. These results, considered in connection with the fact that careful measurements by the moving-boundary method have thus far been made only by two investigators, Denison and Steele, indicate that the values obtained by that method require further confirmation before much confidence can be placed in them. It is to be hoped that the method will be further studied with respect to the sources of error involved and the reproducibility of the same values under varied experimental conditions, for it furnishes by far the most rapid means of determining transference numbers.

It will be seen that in the case of almost all the uni-univalent substances the values obtained by the conductance method at zero concentration agree within about one per cent. with those obtained by the gravimetric method at 0.005 to 0.02 normal. Lithium chloride seems, at first sight, an exception, but not when the rapid change with the concentration is considered.

In the case of uni-bivalent halides, the change with the concentration is so rapid that it is difficult to judge accurately of the correspondence between the results obtained by the two methods. But in the case of the other uni-bivalent salts that have been carefully investigated (potassium sulfate, thallous sulfate, barium nitrate, and lead nitrate at 25°), it is remarkable that though the "gravimetric" values do not change much with the concentration yet they differ by much more than the probable experimental error[2] (namely, by from 9 to 23 $\times 10^{-3}$ units) from the "conductance" values at zero concentration. Moreover, the diver-

[1] These ion-conductances at 18° are nearly identical with those given by Kohlrausch (*Z. Elektrochem.*, 13, 333 (1907)). The small differences arise mainly from the adoption of 0.496 for the transference number of potassium chloride, in place of 0.497, which was used by Kohlrausch.

[2] The probable error in the gravimetric values may be estimated at 2×10^{-3} units in the cases where a weight of 3 or more is assigned. The error in the values with a less weight than 3 is much more difficult to estimate.

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gence is in the same direction for the last three salts, but in the opposit direction for potassium sulfate.

10. Change of the Transference Number with the Concentration and Temperature.

Table VII shows that the transference numbers obtained by the gravimetric method for the uni-univalent substances studied at 18° and at 25° do not vary more than 3×10^{-3} units between the concentrations 0.005 and 0.1 normal, except in the cases of nitric acid and of lithium chloride.

The transference numbers of the halides and sulfates of the bivalent metals (and of lithium chloride) obtained by the gravimetric and moving-boundary methods decrease steadily and rapidly with increasing concentration. This large change is probably due not to physical causes, but to changes in the composition of the ions; thus it may be accounted for by assuming that complex anions, such as $BaCl_4^{=}$ or $Mg(SO_4)_2^{=}$, are formed in considerable quantity at the higher concentrations.

The other uni-bivalent salts (potassium and thallium sulfates and barium and lead nitrates), as above noted, show little, if any, change at concentrations between 0.03–0.05 and 0.1–0.2 normal; but there is a difference of 2 to 5 per cent. between these values and those at zero concentration. This suggests the possibility that the conductance values extrapolated for zero concentration may be considerably in error in the case of these salts—a matter that will be discussed in detail in the third paper.

The fact that the transference numbers of these uni-bivalent salts, unlike the bivalent halides, show little, if any, progressive change with the concentration, makes it probable, though it does not prove,[1] that intermediate ions (such as KSO_4^{-} or NO_3Ba^{+}) and complex ions (such as $K_2(SO_4)_2^{=}$) are not present in large quantities in solutions of these salts, at concentrations up to 0.2 normal.[2]

Hydrochloric acid and sulfuric acid[3] also show a nearly constant transference number between 0.005 or (0.02) normal and 0.1 normal; but there is a considerable difference between the value at these concentrations

[1] See the theoretical discussion of this matter near the end of Section 6 of this article; also Falk, This Journal, 32, 1567–70 (1910).

[2] It is to be noted that, even if the difference between the values at zero and higher concentrations be regarded as real, the change lies (except in the case of potassium sulfate) in a direction opposit to that which would be produced by the presence of the intermediate ion (unless its equivalent conductance be even smaller than that required by equations (21) given in Section 6).

[3] For a full discussion of the transference relations of sulfuric acid, see Noyes and Stewart, This Journal, 32, 1134, 1138 (1910).

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and that at zero concentration. The latter fact becomes especially obvious when one considers the anion-transference numbers, which were the quantities obtained directly from the experiments; thus those for hydrochloric acid are —172 at 0.0 normal and —166 at 0.1 normal. This again suggests an error in the values of the equivalent conductance of the ions at zero concentration. It indicates more specifically, as pointed out by Noyes and Sammet[1] and Noyes and Kato,[2] that the hydrogen-ion at higher concentrations has a considerably higher conductance than that derived from conductance measurements with very dilute acids. The latter authors conclude that this was probably true only at the higher concentrations, and that the conductance of the hydrogen-ion increased markedly with increasing concentration. But in view of the approximate constancy of the transference number between 0.005 and 0.1 normal, which the now available data indicate, it seems more probable that the value for the hydrogen-ion at zero concentration is in error. The transference number of nitric acid, unlike those of hydrochloric and sulfuric acids, increases markedly with increasing concentration.

The change in the transference number taking place at concentrations above 0.1 normal has been carefully investigated for only a few substances. The results may best be seen by reference to Table V. The effect of concentration is pronounced only in the cases of the halides and sulfates of the bivalent metals and of lithium chloride, and is probably due mainly to complex anions, as is illustrated most strikingly by the negative transference of cadmium iodide at 0.5 normal and above. The smaller effects in the other cases are doubtless due, at least, in part, to hydration of the ions, since this has been definitly shown by Washburn to be true for the chlorides of potassium, sodium and lithium.

In regard to the effect of temperature the statement can be made that in the case of the substances investigated the transference number with rising temperature invariably decreases if larger than 500×10^{-3}, and increases if smaller than this quantity, showing that the transference and velocity of the various ion-constituents differ by a smaller fractional amount at the higher temperatures. The transference measurements at different temperatures are not numerous nor accurate enough to warrant other general conclusions of a quantitative character.

BOSTON, MASS.

[1] THIS JOURNAL, 24, 967–8 (1902).

[2] *Ibid.*, 30, 332 (1908).

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[CONTRIBUTIONS FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE LAWS OF "CONCENTRATED" SOLUTIONS: II.[1] THE ESTIMATION OF THE DEGREE OF IONIZATION OF ELECTROLYTES IN MODERATELY CONCENTRATED SOLUTIONS.[2]

BY EDWARD W. WASHBURN.

Received July 15, 1911.

1. Introduction.

The greatest obstacle with which we are confronted, when we attempt to apply, quantitatively, the principles of the Ionic Theory to any except the most dilute solutions, is the lack of a satisfactory method for computing the degree of ionization of an electrolyte in a concentrated solution. Until some method is found or adopted for this purpose no progress into the region of concentrated solutions is possible. It is the purpose of the present paper to examine critically the different methods which are at present in use for calculating the degree of ionization of electrolytes in dilute solutions with the view of deciding what, in the present state of our knowledge, is the best method to employ for this purpose in the more concentrated ones.

For dilute solutions two general classes of methods are employed at present. To the first class belong the so-called "Osmotic" methods—better called the Colligative Property Methods[3]—which involve the knowledge of some colligative property of the solution, such as the freezing point lowering, the boiling point raising, the relative vapor pressure lowering, etc. To this class belongs also the method based upon the e. m. f. of a concentration cell and involving the assumption that the ions are normal solutes.

The second class comprises only the conductivity method of Arrhenius.

2. The Colligative Property Methods for Calculating Degree of Ionization.

The calculation of the degree of ionization of an electrolyte from any one of the colligative properties of its solution is based upon the assumption that both the ions and the unionized molecules are *normal solutes*, that is, that each produces upon the colligative property in question (*e. g.*, the f. p. lowering) the same effect as would be produced by an equal number of molecules of an ordinary non-electrolyte, such as alcohol,

[1] In the first contribution of this series (THIS JOURNAL, 32, 653 and 1636 (1910); also *Z. physik. Chem.*, 74, 537 (1910) and *J. chim. phys.*, 8, 538 (1910)) is presented the outline of a theory of solutions which is free from the assumption that the solution must be dilute. From the point of view of this theory, a systematic investigation of the subject of concentrated solutions has been undertaken in this laboratory and will be pushed as rapidly as the means at our disposal will permit.

[2] Presented at the Indianapolis meeting of the Society, June 29, 1911.

[3] Cf. THIS JOURNAL, 32, 496 (1910) and *Ibid.*, 32, 659 (1910).

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for example; or, in other words, that their active masses, or "Activities"[1] are, in dilute solutions, proportional to their concentrations. This assumption, we know, however, cannot be true, for if it were, the Mass Action Law would be a thermodynamic necessity for a strong electrolyte, that is, failure to obey this law would constitute a real exception to the Second Law of Thermodynamics. This important point, which was emphasized by Jahn[2] in 1904 and to which attention has been recently called by G. N. Lewis,[4] is often overlooked. *When values for the degree of ionization calculated from some colligative property of the solution (e. g., the f. p. lowering) agree with those computed from the conductivity ratio, this agreement is frequently cited as evidence of their correctness. Such a conclusion is, however, not justified, for the colligative property method can only give correct value by an accidental compensation of errors*, the deviations of the ions from the behavior of a normal solute in the one direction being exactly compensated by the deviations of the unionized molecules in the opposit direction.[3]

All the evidence at present available[4] seems to indicate that the ions, of uni-univalent salts, at least, do not deviate widely from the behavior of normal solutes in dilute solution, but that the unionized molecules are very abnormal in this respect. In sufficiently dilute solutions, therefore, where the unionized molecules constitute only a *few per cent.* of the total number of solute molecules, the freezing point lowering should correspond, within a *few per cent.*, with the value calculated by using the conductivity ratio as a measure of the degree of ionization. Whenever, however, the unionized molecules begin to form an appreciable part of the total number of solute molecules, we can no longer estimate correctly the degree of ionization from the freezing point lowering or from any of the other colligative properties thermodynamically connected with it; and this would still be true, even if the complication due to hydration could be eliminated. For the purposes of the present paper, therefore, this method will have to be rejected.

It may be mentioned, in passing, that even in the case of *dilute* solutions of certain electrolytes of a high ionic type, where the degree of ionization is not large, very abnormal results may be obtained. A number of salts of this character have been investigated recently by A. A. Noyes and J. Johnston.[5]

3. The Conductivity Method.

The customary method for calculating the degree of ionization, γ,

[1] Lewis, *Proc. Amer. Acad.*, 43, 288 (1907).

[2] *Z. physik. Chem.*, 50, 152 (1904).

[3] Cf. THIS JOURNAL, 32, 492 (1910).

[4] This evidence is presented by A. A. Noyes in various publications (cf. THIS JOURNAL, 30, 351 (1908).

[5] THIS JOURNAL, 31, 1008 (1909).

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of an electrolyte from conductivity data by means of the equation, $\gamma = \Lambda/\Lambda_0$, is based among others upon the two assumptions: (1) that the physical dimensions of the ions and (2) that the resistance offered to their motion through the solution are constants, not affected by changes in the concentration of the electrolyte.

These two assumptions are justified if the solution be "sufficiently dilute," but the expression, "sufficiently dilute," frequently means much more dilute than are many of the solutions which we are accustomed to regard as "dilute solutions." For example, the above equation is quite generally applied to 0.1 molal solutions and the value for γ expressed to tenths of a per cent. and yet the viscosity of a 0.1 molal solution may differ from that of pure water by *several per cent.*, even in the case of the simplest type of electrolytes. Some examples of the relative viscosities (η/η_0), of some 0.1 molal aqueous solutions are shown in Table I. It is evident from this table that *the neglect of the viscosity influence*

TABLE I.[1]—RELATIVE VISCOSITIES OF SOME 0.1 MOLAL AQUEOUS SOLUTIONS.

Salt.	$CsNO_3$.	$LiIO_3$.	NaOH.	Na_2HPO_4.	NaH_2PO_4.	Na_3PO_4.	Na benzoate.	Na hydrocinnamate.	Na isovalerate.
t.....	0°	18°	18°	18°	18°	18°	25°	25°	25°
η/η_0....	0.98	1.03	1.025	1.07	1.03	1.08	1.05	1.07	1.06

may introduce errors as high as 7 and 8 per cent. in the degree of ionization of a 0.1 molal solution as calculated from the conductivity ratio.[2] *In fact it may be stated as a general rule that the equation $\gamma = \Lambda/\Lambda_0$ cannot be safely employed for solutions of greater concentrataions than 0.01 molal, if an accuracy of a few tenths of a per cent. is desired.*

Even in the case of a 0.01 molal solution the influence of the viscosity effect is sometimes surprizingly large. The error from this source is about one-tenth of the error in the case of the 0.1 molal solution and may therefore in some cases amount to nearly one per cent., as is evident from Table I.

It is clear therefore that, in the case of all solutions of higher concentrations than 0.01 molal, it is necessary to take into account the viscosity of the solution in computing the degree of ionization of the electrolyte. The remainder of this communication will be devoted chiefly to the consideration of the best method of applying the viscosity correction. The influence of changes in the physical dimensions of the ions will also re-

[1] Compiled from existing data in the literature.

[2] The very high viscosities of the solutions of the sodium salts of the phosphoric acids are of especial importance in connection with the investigation by Abbott and Bray (THIS JOURNAL, 31, 729 (1909)) of the equilibria and ionization relations in solutions of these acids and their salts. For a 0.1 molal solution of Na_2HPO_4 Abbott and Bray calculate the degree of ionization to be 0.596, *a result which is probably in error by more than per cent.* Their calculations are in need of revision, owing to the unusually large influence of the viscosity factor for these solutions.

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ceive consideration in Section 7. This latter influence is one of the chief determining factors in very concentrated solutions and is closely connected with the cause of the minima frequently observed in the equivalent conductance curves.[1] There is at present no known method of estimating and correcting for this effect so that any method for computing degree of ionization in concentrated solutions must be restricted to solutions of moderate concentrations, say not exceeding normal, where this influence may be safely neglected.

4. The Viscosity Correction.

The ions and unionized molecules of a dissolved electrolyte, both directly by their own presence and indirectly through their effect upon the degree of association of the water, produce a medium whose viscosity is different from that of pure water. The change in viscosity may be either an increase or a decrease but for nearly all solutions of salts of inorganic acids, the magnitude of this change will not be greater than 40 per cent., for concentrations not exceeding one equivalent of salt per liter.[2] The relative viscosities of such solutions will be included between the limits 0.8 and 1.4.

In order to correct for the change in the mobilities of the ions produced by a change in the viscosity of the medium, the simplest assumption to make is that the mobility of an ion is inversely proportional to the viscosity, η, or directly proportional to the fluidity, f, of the medium. On the basis of this assumption the equation for the degree of ionization becomes

$$\gamma = \frac{\Lambda\eta}{\Lambda_0\eta_0} \text{ or } \gamma = \frac{\Lambda f_0}{\Lambda_0 f}. \qquad (1)$$

This equation has been proposed and employed by several authors[3] as a measure of ionization, a procedure which is unquestionably more logical than the entire neglect of the viscosity influence. Moreover, if we make certain assumptions, equation (1) can be derived theoretically from Stokes' equation for the motion of a small sphere through a viscous medium. The necessary assumptions are those which Stokes made in deriving his equation from the principles of the kinetic theory; namely, that the moving body (the ion in the present instance) must be a sphere and that its volume

[1] See, for example, Sloan's curve for potassium iodide solutions at 0° (THIS JOURNAL, 32, 946 (1910).

[2] In addition to their effect upon the viscosity, the presence of unionized molecules in sufficient number may increase the conductivity through a kind of Grotthus-Chain action, but if their number does not exceed those present in a normal solution of a strong electrolyte, this effect will probably be very small. At all events it will be neglected in what follows, as there is at present no way of applying any correction for it.

[3] Cf. Sutherland, *Phil. Mag.*, [6] 3, 161 (1902); Bousfield and Lowry, *Phil. Trans. Roy. Soc. London* (*A*), 204, 256 (1905); Bousfield, *Z. physik. Chem.*, 53, 257 (1905) and *Phil. Trans.* (*A*), 206, 101 (1906).

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must be large in comparison with the volume of the molecules of the medium through which it moves.

Neither of these conditions is in general fulfilled by the ions of electrolytes, so that exact proportionality between ionic mobility and fluidity is not to be expected and although the deviations should not be very great they may nevertheless be quite appreciable and should, if possible, be taken into account in correcting for the viscosity influence. That appreciable deviations are to be expected has been demonstrated theoretically by Cunningham,[1] and Millikan[2] has recently succeeded in demonstrating such deviations experimentally in the case of gaseous ions collected on very minute oil drops.

These considerations together with certain relationships discovered by W. H. Green[3] and by J. Johnston[4] have led the writer to adopt provisionally the following principle as furnishing, for the formulation of the viscosity correction, for moderately concentrated solutions, a more logical basis than Stokes' law.

The mobility of an electrolytic ion is in the case of salts[5] *proportional to the mth power of the fluidity of the medium through which it is moving, the coefficient, m, being not far from unity.*

The evidence in favor of the adoption of this principle is contained in or can be obtained from the papers of Green and Johnson above mentioned. We shall proceed to the consideration of the work of each investigator separately.

The Experiments of W. H. Green.—The purpose of these experiments is sufficiently evident from the title of the paper[3] and they constitute the most valuable direct contribution to the problem which has yet been made. "The problem was attacked experimentally by adding a non-electrolyte to a solution of a good electrolyte so as to cause artificially a considerable decrease in the fluidity. Simultaneous observations of both conductivity and fluidity were made." The solutes employed were lithium chloride and sucrose.

The measurements include a wide range of concentrations of both lithium chloride and sucrose, and were sufficiently extensive to enable extrapolations to be made in such a way as to give a set of equivalent conductance data for solutions of various fluidities (and therefore of dif-

[1] Cunningham, *Proc. Roy. Soc. London* (*A*), 83, 357 (1910).

[2] Millikan, *Physic. Rev.*, 32, 349 (1911).

[3] W. H. Green, "Studies on the Viscosity and Conductivity of Some Aqueous Solutions.....A Contribution towards the Elucidation of the Connection between Ionic Mobility and the Fluidity of the Solution" (*J. Chem. Soc.*, 93, 2049 (1908)).

[4] J. Johnston, "The Change of the Equivalent Conductance of Ions with the Temperature" (THIS JOURNAL, 31, 1010 (1909)).

[5] This principle does not seem to hold for the mobilities of hydrogen- or hydroxyl-ions so that acids and alkalies are not included in what follows. See Section 9.

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ferent sucrose concentrations) but of infinit dilution with respect to lithium chloride. It is with these results that we are chiefly concerned, since they permit of a direct comparison of ionic mobility and fluidity without the interference of an unknown ionization factor.

The data necessary for this comparison are shown in Table II. With the exception of column VII, these figures are taken directly from Table VII of Green's paper; with reference to the figures in columns V and VI Green says: "It will be observed that Λ is by no means proportional to f but more nearly to $f^{0.7}$." This latter "proportionality" is not a very satisfactory one, however. This is evident from the figures in column VI and can be seen graphically if values of $log\ \Lambda$ are plotted against values of $log\ f$, since if $\Lambda = kf^m$, then $log\ \Lambda = log\ k + m\ log\ f$, and the graph should be a straight line. Such a plot was made on a large scale, and showed clearly that the relation between $log\ \Lambda$ and $log\ f$ is not a linear one.

TABLE II.

Temperature 25°.

I. Number.	II. Mols. of sucrose per liter of solution. N.	III. Fluidity in absolute units. f.	IV. Equivalent conductance of LiCl at infinit dilution. Λ_0	V. Λ_0/f.	VI. $\Lambda_0/f^{0.7}$.	VII. $\Lambda_0/f^{0.94}$.
1	0	111.67	114.0	(1.020)[1]	...	1.37
2	0.02	109.75	111.84	1.019	4.169	1.37
3	0.05	107.00	108.85	1.017	4.132	1.36
4	0.1	102.40	104.15	1.017	4.078	1.36
5	0.2	93.42	95.80	1.025	4.000	1.35
6	0.4	76.43	81.05	1.060	3.895	1.39
7	0.6	61.06	68.67	1.125	3.862	1.44
8	0.8	47.51	56.85	1.197	3.811	..
9	1.0	35.91	46.62	1.298	3.802	..
10	1.2	26.28	37.38	1.422	3.793	..
11	1.4	18.57	29.50	1.588	3.815	..
12	1.6	12.54	22.72	1.812	3.870	..
13	1.8	8.017	16.83	2.099	3.920	..
14	2.0	4.826	12.02	2.490	3.993	..

The deviation from linearity is in the direction of a too rapid increase in Λ with increasing concentration of sucrose. A deviation in this direction in the more concentrated solutions, however, might be expected. Owing to the high degree of hydration of both the chloride and the lithium ions, especially the latter,[2] their volumes would decrease with increasing concentration of sucrose, owing to the decrease in their degrees of hydration. This would cause an increase in their mobilities for a given viscosity and a consequent too rapid increase in Λ exactly as observed.

[1] This value net given in Green's table.

[2] Green seems inclined (*Loc. cit.*, p. 2061) to reject the theory that ions are hydrated.

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It should be further noted that between pure water and the twice molal sucrose solution, there is a decrease of 96 per cent. in the fluidity of the medium. Over such an enormous range as this the simple exponential law may be insufficient to express the relationship between ionic mobility and fluidity, even if the ionic volumes remain constant. For the purposes of the present paper it will be sufficient if we can show that the simple exponential law is sufficiently exact for the range of fluidities included between that of pure water and those of normal salt solutions.

In order to test this for LiCl, using Green's data, the large scale plot of *log* Λ against *log* f was employed. The first six points (numbers 1 to 6 inclusive of Table II), that is up to and including the 0.4 normal sugar solution, involve a decrease of about 32 per cent. in the fluidity. Through these six points the "best straight line" was drawn. The location of this line was established independently by five different men and the following values for its slope were obtained: m = 0.940, 0.939, 0.934, 0.918, 0.958; mean[1] 0.94 ± 0.01.

The relation between Λ and f is, therefore, $\Lambda = k\, f^{0.94}$. In column VII of Table II are shown values of $\Lambda/f^{0.94}$ for the first seven solutions.[2]

[1] If the first five points only are used, the value m = 0.97 is obtained. An uncertainty in m, of this magnitude (0.03), would mean an error of only 0.4 per cent. in the value of γ, for a normal LiCl solution at 25° (see p. —).

[2] With reference to the bearing of his experiments upon the question of calculating the degree of ionization, Green's final conclusion is that: "No trustworthy method has as yet been established whereby the true ionization coefficients of a salt in solution can be determined." His basis for this conclusion seems to have been chiefly the fact that the ionization-coefficients which he obtained seemed to indicate that the degree of ionization of lithium chloride is "enormously increased" by the addition of sucrose. His ionization coefficients were obtained by dividing the equivalent conductance of the solution by the equivalent conductance of a solution infinitly dilute with respect to lithium chloride but which contained sufficient sucrose to give it the same fluidity as the first solution. The following examples will illustrate the character of the results thus obtained:

1. A 0.5 normal solution of LiCl in water contains 108 mols. of H_2O per mol. of LiCl and has Λ = 82.28 and f = 104.35. A sucrose solution which has this fluidity contains 0.08 mol. of sucrose per 1000 grams or 0.17 mol. per 108 mols. of water and has Λ_0 = 106.2. The ionization coefficient of the first solution is therefore 82.3/106.2 = 0.775.

2. A solution 0.5 normal with respect to LiCl and 0.1 normal with respect to sucrose contains 107 mols. of water and 0.2 mol. of sucrose per mol. of LiCl and has Λ = 77.3 and f = 94.8. A sucrose solution which has this fluidity contains 0.37 mol. of sucrose per 107 mols. of water and has Λ_0 = 97.2. The ionization-coefficient for the second solution is therefore 77.3/97.2 = 0.795.

3. A solution 0.5 normal with respect to LiCl and 1 normal with respect to sucrose contains 86 mols. of water and 2 mols. of sucrose per mol. of LiCl and has Λ = 37.06 and f = 34.30. A sucrose solution which has this fluidity contains 2 mols. of sucrose per 86 mols. of water and has Λ_0 = 43.1. The coefficient of ionization of the third solution is therefore 37.06/43.1 = 0.86.

Similarly a 0.05 normal solution of LiCl in water is about 88.5 per cent. ionized,

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The Change of the Equivalent Conductance of Ions with the Temperature.—Instead of altering the fluidity of the medium by the addition of a third substance to the solution, as in Green's experiments, we can bring about the change in fluidity by simply altering the temperature. In attempting to find a function connecting ionic conductances and temperature, which could be used advantageously for interpolation, J. Johnston noticed that if the logarithms of the Λ_0 values (for a given ion or for a given salt) were plotted against the logarithms of the fluidity of water corresponding to each temperature, the resulting graph was a straight line. In other words when the fluidity of the medium is altered by a change in temperature, the mobility of an ion changes according to the law, $\Lambda_0 = kf_0^{\,m}$.

Johnston found that this relation was satisfied for the temperature range 0° to 156° in the case of fourteen different ions. In Table III are shown the values of the exponent m for the univalent ions. With the exception of the values for Cs and Li which have been computed by the writer, these figures are taken from Table 4 of Johnston's paper.

TABLE III.

Ion.	Cs.	K.	NH_4.	Na.	Li.	Ag.	NO_3.	Cl.	$C_2H_3O_2$.
m.....	0.842	0.887	0.891	0.97	1.05	0.949	0.807	0.88	1.008

The values for Cs and Li are based upon conductance and viscosity data at 0° and 18° only, no measurements at higher temperatures being available.

A glance at this table suggests several interesting relations: (1) In no instance does the value of m differ from unity by as much as 0.2. (2) In the case of the alkali ions the exponent m increases with increasing ionic volume being smallest in the case of the (probably) unhydrated Cs ion and greatest in the case of the highly hydrated Li ion. (3) K-ion and Cl-ion which have nearly the same ionic volumes have also the same value for m. (4) The value for the very large Li-ion is greater than unity. These ions probably resemble most nearly the minute spheres studied by Millikan, and the deviation from Stokes' law is in the same direction as that which he observed. In the case of the other ions their possibly unsymmetrical shape and their much smaller size in comparison with the water molecules combine to produce a smaller increase of mobility with increasing fluidity, than Stokes' law requires.

Using the data of Dutoit and Duperthuis[1] on the fluidity and the con-

while the presence of 0.01, 0.1 and 1 mols. respectively of sucrose per liter of solution apparently increases the per cent. of ionization to 89.4, 92.6 and 97.5 respectively.

When we consider the high degrees of hydration of both the lithium chloride and the sucrose and the variations in the vapor pressure of the water in the above cases, it does not seem to the writer that Green's conclusion is unavoidable. A similar investigation with caesium nitrate or iodide as the electrolyte would be very valuable, because the complications due to hydration would be eliminated.

[1] *J. chim. phys.*, 6, 726 (1908).

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ductances at zero concentration of sodium iodide in a number of solvents at a series of temperature between 0° and 80°, Johnston applied the equation $\Lambda_0 = kf_0^m$, and found that it agreed with the observations in every instance. The values of m for the different solvents were as follows: Ethyl alcohol, 0.935; propyl alcohol, 0.974; isobutyl alcohol, 0.955; isoamyl alcohol, 0.806; acetone, 1.086; and pyridine, 0.99.

In the opinion of the writer the foregoing evidence justifies the adoption of the relation, $\Lambda = kf^m$, as a basis for applying the viscosity correction in calculating the degree of ionization of univalent salts, up to a concentration of one equivalent per liter, at least. In the next section the method of applying this correction in practice will be discussed.

5. Application of the Viscosity Correction in Practice.

The method of applying the viscosity correction in practice is based upon the fact that if the equation $\Lambda = kf^m$ is applicable to the equivalent conductance of an ion it may, in very many cases, be applied to the equivalent conductance of a salt as well. Johnston found this to be the case for the salts investigated by him, and we have seen that it is also true in the case of Green's experiments with lithium chloride. It can also be shown to follow mathematically, as will be evident from the following derivation of the expression for the degree of ionization, γ.

Consider a salt of the type KA in aqueous solution at a concentration not greater than normal. Let the fluidity of the solution be f, the degree of ionization be γ, and the equivalent conductance, $\Lambda = \Lambda_K + \Lambda_A$. Similarly at zero concentration we have the fluidity f_0 and the equivalent conductance, $\Lambda_0 = \Lambda_{0_K} + \Lambda_{0_A}$. We have also for the individual ions the two equations $\Lambda_{0_K} = k_K f_0^{m_K}$ and $\Lambda_{0_A} = k_A f_0^{m_A}$ from which it follows that

$$\Lambda_K = \gamma \Lambda_{0_K}\left(\frac{f}{f_0}\right)^{m_K} \quad (2) \qquad \text{and} \qquad \Lambda_A = \gamma \Lambda_{0_A}\left(\frac{f}{f_0}\right)^{m_A}. \quad (3)$$

Adding these last two equations together and solving for γ we obtain the equation

$$\gamma = \frac{\Lambda}{\Lambda_{0_K}\left(\frac{f}{f_0}\right)^{m_K} + \Lambda_{0_A}\left(\frac{f}{f_0}\right)^{m_A}} \quad (4)$$

which, by a simple algebraic transformation, may be written as follows:

$$\gamma = \frac{\Lambda}{\Lambda_0}\left(\frac{f}{f_0}\right)^m \left[\frac{\Lambda_0}{\Lambda_{0_K}\left(\frac{f}{f_0}\right)^{m_K - m} + \Lambda_{0_A}\left(\frac{f}{f_0}\right)^{m_A - m}}\right] \quad (5)$$

where m has a value intermediate between m_K and m_A. Now if f/f_0 lies between 0.8 and 1.4 (as it does in the case of nearly all salt solutions of concentrations not greater than normal) and since m, m_A and m_K are not far from unity, the expression in the brackets will in most instances

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also be equal to unity within about 0.1 of a per cent. Two examples will serve to illustrate this.

For 0.5 N lithium chloride at 0° the expression in the brackets becomes

$$\frac{60.30}{19.2(0.9)^{[1.05-0.94=0.11]} + 41.1(0.9)^{[0.88-0.94=-0.06]}} = 0.9995$$

and for 0.5 N cesium nitrate at 0° it becomes

$$\frac{84.0}{43.7(1.1)^{[0.482-0.826=0.016]} + 40.3(1.1)^{[0.807-0.826=-0.02]}} = 1.00008.$$

The expression for γ may therefore be written

$$\gamma = \frac{\Lambda}{\Lambda_0}\left(\frac{f_0}{f}\right)^m \tag{6}$$

or in terms of viscosity

$$\gamma = \frac{\Lambda}{\Lambda_0}\left(\frac{\eta}{\eta_0}\right)^m. \tag{7}$$

Stated in words, *the degree of ionization is equal to the equivalent conductance ratio multiplied by the relative viscosity of the solution raised to the m-th power.*

Equation (6) also means that the relation $\Lambda = kf^m$ holds for the equivalent conductance of a *salt* as well as for the equivalent conductance of an *ion*. In the case of some salts, however, in which a high viscosity of the solution is accompanied by a comparatively large difference between m and either m_K or m_A, this may not be true. In such a case it would be necessary to determin the separate values of m_A, m_K, Λ_{0_A} and Λ_{0_K} and employ the more exact equation, (4), for calculating γ. This will be seldom necessary, however.

The most convenient way in which to determin the numerical value of the fluidity exponent, m, for any given salt is to make use of Λ_0 and f_0 values for the salt at two temperatures, preferably two temperatures equally distant from and not very far from the temperature at which γ is desired. This latter stipulation is not very essential, however, in most cases, since the value of m for most salts will be nearly independent of the portion of the temperature scale employed, as Johnston's calculations show. In the case of a highly hydrated salt, however, it is desirable to use as small a temperature interval as possible and to restrict it to the neighborhood of the temperature at which γ is desired.

The Accuracy Necessary in the Value of m.—If γ is desired with a percentage accuracy of $100\delta\gamma/\gamma$ then the accuracy with which m must be known is obtained as follows:

$$\gamma = \frac{\Lambda}{\Lambda_0}\left(\frac{\eta}{\eta_0}\right)^m \tag{8}$$

$$\delta\gamma = \frac{\Lambda}{\Lambda_0}\log_e\frac{\eta}{\eta_0}\cdot\left(\frac{\eta}{\eta_0}\right)^m\delta m \tag{9}$$

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and

$$\frac{100\delta\gamma}{\gamma} = 100 \log_e \left(\frac{\eta}{\eta_0}\right)\delta m \qquad (10)$$

Expanding the logarithm and rejecting all except the first term, we have,

$$\frac{100\delta\gamma}{\gamma} = 100\left[\frac{\eta}{\eta_0} - 1\right]\delta m \qquad (11)$$

or

$$\delta m = \frac{100\delta\gamma}{\gamma} \Big/ 100\left[\frac{\eta}{\eta_0} - 1\right]. \qquad (12)$$

If η/η_0 lies between 0.8 and 1.4, m need not be determined with an accuracy of more than 1/40 ($100\delta\gamma/\gamma$) units and usually an accuracy of 1/20 ($100\delta\gamma/\gamma$) units will be sufficient. For example, if γ is desired to 0.1 per cent., then an error in m of 1 in the second decimal place will usually be allowable and sometimes a much larger error is permissible. The following examples illustrate this. A desired accuracy of 0.1 per cent. in γ is assumed.

(1) For a half normal cesium nitrate solution at 0°, $\eta/\eta_0 = 0.9$, and $m = 0.826$ with an allowable error of 1 in the second decimal place.

(2) For a normal potassium chloride solution at 18°, $\eta/\eta_0 = 0.985$, and $m = 0.905$ with an allowable error of 7 *in the second decimal place.*

(3) For a normal lithium chloride solution at 25°, $\eta/\eta_0 = 1.15$ and $m = 0.940$ with an allowable error of 7 in the third decimal place.

Since m is determined from Λ_0 values and f_0 values at two different temperatures, $t_1°$ and $t_2°$, it is important to know how far apart these two temperatures must be taken in order to give m with s ient accuracy. This problem can be solved as follows.

The Temperature Interval Necessary for Computing m.—For m we have the expression

$$m = \frac{\log \Lambda_{0_1} - \log \Lambda_{0_2}}{\log \frac{f_{0_1}}{f_{0_2}}} \qquad (13)$$

in which the subscripts 1 and 2 refer to the two temperatures $t_1°$, and $t_2°$. f_1 and f_2 may be assumed to be known to any desired accuracy, since the error in m will be due almost entirely to the errors in the Λ_0 values. By the method of Least Squares we have therefore

$$\delta m = \frac{1}{\log \frac{f_{0_1}}{f_{0_2}}} \sqrt{\left(\frac{\delta\Lambda_{0_1}}{\Lambda_{0_1}}\right)^2 + \left(\frac{\delta\Lambda_{0_2}}{\Lambda_{0_2}}\right)^2} \qquad (14)$$

and assuming the same fractional accuracy in both of the Λ_0 values

$$\delta m = \frac{\delta\Lambda_0}{\Lambda_0} \frac{\sqrt{2}}{\log \frac{f_{0_1}}{f_{0_2}}}. \qquad (15)$$

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Combining with equation (10) on page 1471 we obtain

$$\log \frac{f_{o_1}}{f_{o_2}} = \frac{\sqrt{2}\,\frac{\delta \Lambda_o}{\Lambda_o}\left(\frac{\eta}{\eta_o} - 1\right)}{\frac{\delta \gamma}{\gamma}}. \qquad (16)$$

Thorpe and Rodger found that their results for the viscosity of water at temperatures up to 100° could be expressed by a formula which may be written in the following form:

$$\log f = 1.5423 \log (43.252 + t) + \text{const.} \qquad (17)$$

from which follows the equation

$$\log \frac{f_{o_1}}{f_{o_2}} = 1.5423 \log \frac{43.3 + t_1}{43.3 + t_2}. \qquad (18)$$

Combining this equation with equation (16), we obtain

$$\log \frac{43.3 + t_1}{43.3 + t_2} = \frac{\sqrt{2}}{1.54}\left(\frac{\eta}{\eta^o} - 1\right)\frac{\delta \Lambda^o}{\Lambda_o} \Big/ \frac{\delta \gamma}{\gamma}. \qquad (19)$$

Expanding the logarithm and rejecting negligible quantities, we obtain the expression

$$\frac{t_1 - t_2}{43 + t_2} = 0.92\,(\eta/\eta_o - 1)\,\frac{\delta \Lambda_o}{\Lambda_o} \Big/ \frac{\delta \gamma}{\gamma}. \qquad (20)$$

Now the value of $\delta\gamma/\gamma$ can never exceed that of $\delta\Lambda_o/\Lambda_o$, so that since we desire a minimum value for $t_2 - t_1$, we may place $\delta\gamma/\gamma = \delta\Lambda_o/\Lambda_o$. Also the temperatures t_2 and t_1 should preferably be equidistant from the temperature, t, at which γ is desired, so that for t_2 in the denominator of the left-hand member of the above equation, we may write $t + 1/2(t_2 - t_1)$. Making these changes our equation becomes, finally,

$$t_2 - t_1 = \frac{(86 + 2t)(\eta/\eta_o - 1)}{1.2 + \eta/\eta_o}. \qquad (21)$$

Thus, if t is in the neighborhood of 0°, the temperature interval necessary to determin m need not exceed 13°, if $t = 25°$ it need not exceed 20°, and if $t = 50°$ it need not exceed 30°. In most cases a much smaller interval will be sufficient.

In this calculation we have assumed that the Λ_o values at $t_1°$ and $t_2°$, the two temperatures employed for calculating m, are known with the same percentage accuracy as the Λ_o value at $t°$, the temperature at which γ is desired. If such is not the case the value of $t_2 - t_1$, obtained from equation (21), must be multiplied by

$$\sqrt{\left(\frac{\delta \Lambda_{o_1}}{\Lambda_{o_1}}\right)^2 + \left(\frac{\delta \Lambda_{o_2}}{\Lambda_{o_2}}\right)^2} \Big/ \frac{\delta \gamma}{\gamma}.$$

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6. Examples Illustrating the Results Obtained from the Equation, $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$.

In order to illustrate the character of some of the results obtained by the use of the above expression in the case of moderately concentrated aqueous salt solutions, it will be applied to solutions of caesium nitrate, potassium chloride and lithium chloride at 0°. The conductance and viscosity data necessary for these calculations have been obtained in this laboratory by Dr. D. A. MacInnes and will be published in full in the November Journal in connection with the third paper of this series.

In order to calculate values for the fluidity exponent, m, for these three salts, conductance and fluidity data at 0° and 18° were employed. They are shown in Table IV, together with the values for m which they give. The values of f_0 at the two temperatures are those of Thorpe and Rodger as corrected by Green.[1] The values of Λ_0 for cesium nitrate and lithium chloride at 0° were determined by MacInnes.

TABLE IV.

	0°.		19°.		
	Λ_0.	f_0.	Λ_0.	f_0.	m.
$CsNO_3$	84.0	...	129.9	...	0.826
KCl	81.0	...	130.2	...	0.900
LiCl	60.3	...	98.93	...	0.940
H_2O	..	0.01792	..	0.01058	...

The Λ_0 value for potassium chloride is from an extrapolation based upon the data of several observers. The Λ_0 values for 18° are those of Kohlrausch corrected to the basis of the 1910 atomic weights.

In Tables V to VII are shown values of η/η_0, Λ, Λ/Λ_0, $\Lambda\eta/\Lambda_0\eta_0$, and $\Lambda/\Lambda_0(\eta/\eta_0)^m$ for these three salts at 0° for a number of concentrations up to $n' = 0.5$ equivalent per 1000 grams of water. These illustrate the magnitude and direction of the viscosity correction in the case of typical uni-univalent salts of inorganic acids. Thus, the values for the per cent. of ionization of cesium nitrate, potassium chloride and lithium chloride, respectively, are altered by the following amounts: for $n' = 0.025$ by 0.1, 0.1 and 0.3 per cent.; for $n' = 0.1$ by 1.2, 0.3 and 1 per cent.; and for $n' = 0.5$ by 6.8, 3.8 and 4.6 per cent., respectively.

TABLE V.—CESIUM NITRATE SOLUTIONS AT 0.000°.

n.	η/η_0.	Λ.	Λ/Λ_0.	$\Lambda\eta/\Lambda_0\eta_0$.	$\Lambda/\Lambda_0(\eta/\eta_0)^{0.826}$.
0	1.0000	84.0 ± 0.2	1.000	1.000	1.000
0.025	0.9960	75.19	0.8948	0.8912	0.8939
0.050	0.9905	72.94	0.8680	0.8597	0.8651
0.10	0.9796	69.32	0.8249	0.8080	0.8148
0.20	0.9613	65.18	0.7757	0.7456	0.7543
0.50	0.9138	59.31	0.7058	0.6449	0.6582

[1] Green, *J. Chem. Soc.*, 93, 2029 (1908).

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TABLE VI.—POTASSIUM CHLORIDE SOLUTIONS AT 0.000°.

n.	η/η_0.	Λ.	Λ/Λ_0.	$\Lambda/\Lambda_0\ \eta/\eta_0$.	$\Lambda/\Lambda_0\ (\eta/\eta_0)^{0.90}$.
0.00	1.000	81 ± 0.2	1.00	1.00	1.00
0.025	0.9986	75.6	0.934	0.933	0.933
0.05	0.9974	73.9	0.911	0.908	0.909
0.10	0.9946	71.5	0.882	0.878	0.879
0.20	0.9865	69.1	0.853	0.842	0.842
0.50	0.9571	66.6	0.822	0.786	0.791

TABLE VII.—LITHIUM CHLORIDE SOLUTIONS AT 0.000°.

n.	η/η_0.	Λ.	Λ/Λ_0.	$\Lambda/\Lambda_0\ \eta/\eta_0$.	$\Lambda/\Lambda_0\ (\eta/\eta_0)^{0.94}$.
0	1.000	60.3 ± 0.3	1.000	1.000	1.000
0.025	1.0028	54.54	0.9043	0.9068	0.9067
0.050	1.0056	52.96	0.8781	0.8830	0.8828
0.10	1.0116	51.07	0.8468	0.8565	0.8559
0.20	1.0256	48.39	0.8023	0.8232	0.8219
0.50	1.0694	44.00	0.7296	0.7802	0.7771

7. The Influence of Changes in the Physical Dimensions of the Ions.

At a sufficiently high temperature (209°) and pressure water and liquid silver nitrate are miscible in all proportions and it is, therefore, possible to pass continuously from an infinitly dilute solution of this salt in water to an infinitly concentrated one, that is, to the pure fused salt. As the concentration of the aqueous salt solution increases, the ions gradually lose their water of hydration and take on the character of the ions of the fused salt. These latter may, of course, be surrounded by an envelope of the unionized salt molecules.

These changes in the nature of the ions will, of course, produce corresponding changes in their mobilities and consequently in the conductance of the solution. These will be superimposed upon those resulting from the variation of the viscosity of the medium and, in so far as they are appreciable, will produce an error in the value of γ as calculated from the relation $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$. The magnitude of this error will vary with the nature of the salt and with its concentration, being greatest in the case of the highly hydrated salts and increasing with the concentration. For normal solutions of most inorganic salts the evidence at present available, although rather meager, indicates that the error from this source will not amount to more than about one per cent., except possibly in the case of a highly hydrated salt such as lithium chloride.

In order to be more certain upon this point, it will be necessary to determin the value of the fluidity exponent, m, for a number of salts both by the method of altering the temperature and by the method of adding different non-electrolytes to the solution, as in Green's experiments with lithium chloride and sucrose. Alteration of the pressure at constant temperature also offers a method for calculating m. If the value of m is found to be reasonably independent of the nature of the non-electrolyte

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used to produce the viscosity change, and is also found to be substantially identical with the value obtained by the method of altering the temperature or the pressure, then we may feel reasonably certain that the relation $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$ will give correct results.

At present, data for making such a comparison are available only for one salt, lithium chloride. We have seen above (p. 1469 and Table II) that if the Λ_0 value of this salt is altered by adding sucrose to the solution, the relation between Λ_0 and the fluidity can be satisfactorily expressed by the equation $\Lambda_0 = kf^m$. This equation was found to hold over a range involving a decrease of 32 per cent. in the fluidity and the value of m was found to be 0.94 ± 0.01. We can also calculate the value of m for this salt by the method of changing the temperatures. Between 18° and 0° the fluidity of water decreases 41 per cent. If we calculate the value of m from Λ_0 and f_0 values at 18° and 0° we obtain the result $m = 0.940$, as given in Table III.

The relation $\Lambda = kf^m$ may be also studied by comparing the value of the true transference number calculated from it with the value obtained by direct measurement.

8. The Calculation of True Transference Numbers by Means of the Relation $\Lambda = kf^m$.

The true transference number n of an ion may be defined as equal to the equivalent conductance of the ion divided by that of the ionized salt, or more generally by the sum of the equivalent conductances of all the ions present in the solution. Thus the transference number of the anion of a salt is expressed by the equation

$$n_A = \frac{\Lambda_A}{\Lambda_A + \Lambda_K}. \tag{22}$$

Since the equivalent conductances of different ions change with the viscosity at different rates, it is obvious that the transference number will be a function of the viscosity and if the relation $\Lambda = kf^m$ is correct, we can obviously calculate the true transference number of an ion in any given solution, provided we know its value in any other solution whose relative viscosity with respect to the first solution is known.

To illustrate this we will derive the expression which connects the true transference number of the anion of a salt in a solution whose relative viscosity is η/η_0 with its value at infinit dilution at the same temperature.

The relation $\Lambda = kf^m$ gives us the two equations

$$\Lambda_A = \Lambda_{0A}\left(\frac{f_0}{f}\right)^{m_A} \tag{23}$$

and

$$\Lambda_K = \Lambda_{0K}\left(\frac{f_0}{f}\right)^{m_K}. \tag{24}$$

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Dividing the first of these equations by their sum, we have

$$n_A = \frac{\Lambda_A}{\Lambda_A + \Lambda_K} = \frac{\Lambda_{o_A}}{\Lambda_{o_A} + \Lambda_{o_K}\left(\frac{\eta}{\eta_o}\right)^{m_A - m_K}}. \qquad (25)$$

By an algebraic transformation this equation may be written

$$n_A = \frac{\Lambda_{o_A}}{\Lambda_{o_A} + \Lambda_{o_K}}\left(\frac{\eta}{\eta_o}\right)^{m_A - m} \cdot \left[\frac{\Lambda_o}{\Lambda_{o_A}\left(\frac{f}{f_o}\right)^{m_A - m} + \Lambda_{o_K}\left(\frac{f}{f_o}\right)^{m_K - m}}\right] \qquad (26)$$

in which m, as before, is the fluidity exponent for the salt. The expression in brackets is identical with that in equation (5), which we have seen may be placed equal to unity if (η/η_o) is not very far from unity. For most cases, therefore, equation (26) may be written

$$n_A = n_{o_A}\left(\frac{\eta}{\eta_o}\right)^{m_A - m} \qquad (27)$$

or in words: *The true transference number of an ion in a solution of concentration C is equal to the transference number at infinit dilution multiplied by the relative viscosity of the solution raised to a power equal to the difference between the fluidity exponent of the ion and the fluidity exponent of the salt.*

Since the value of m lies between m_A and m_K, the exponent in the above equation will be positive for the slower ion and negative for the faster ion, so that with decreasing viscosity the transference numbers tend to approach 0.5, a well known tendency which is observed as the temperature increases.

We will now compare the values of the true transference numbers calculated from our equation (27) with those obtained by direct measurement in concentrated solutions. In a previous investigation[1] by the writer, the true transference numbers for 1.2 molal solutions of potassium chloride, sodium chloride and lithium chloride at 25° were measured by transference experiments in the presence of raffinose as a reference substance. Each solution was 0.1 molal with respect to raffinose and the solutions had the following[2] relative viscosities at 25°; LiCl, 1.4; NaCl, 1.3; KCl, less than 1.3. For the transference number of the anion at infinit dilution at this temperature we have,[3] for KCl,

[1] THIS JOURNAL, 31, 322 (1909).

[2] Recent measurements in this laboratory by Mr. L. F. Nickell.

[3] With the exception of the value 38.3 for Li-ion all of these conductance values are taken from the table computed by Johnston (THIS JOURNAL, 31, 1015 (1909)). The value for Li-ion was computed from the data of Green (*J. Chem. Soc.*, 93, 2060 (1908)) and those of Hartley, Thomas and Appleby (*J. Chem. Soc.*, 93, 552 (1908)). For LiCl at 25° Green found $\Lambda_o = 114$. This gives for the conductance of Li-ion, $\Lambda_{o_{Li}} = 114 - 75.5 = 38.5$. Hartley, Thomas and Appleby found for $LiNO_3$ at 25.08°, $\Lambda_o = 109.4$ which for 25° would be 108.8. Using Johnston's Λ_o value for NO_3-ion at this temperature we have $\Lambda_{o_{Li}} = 108.8 - 70.6 = 38.2$.

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$$n_{o_A} = \frac{\Lambda_{o_A}}{\Lambda_{o_A} + \Lambda_{o_K}} = \frac{75.5}{75.5 + 74.5} = 0.504; \qquad (28)$$

for NaCl,

$$n_{o_A} = \frac{75.5}{75.5 + 50.9} = 0.597; \qquad (29)$$

and for LiCl,

$$n_{o_A} = \frac{75.5}{75.5 + 38.3} = 0.664. \qquad (30)$$

The fluidity exponent for Cl-ion is 0.88 (see Table III) and for the three salts it has the following values: for KCl, 0.88; for NaCl, 0.92; and for LiCl, 0.94. Substituting all of the foregoing values in equation (27), we obtain for the true transference number of the chloride ion in the solutions with which direct transference experiments were made by the writer, the following values:

$$\text{For KCl,} \quad n_{Cl^-} = 0.504\ (\eta/\eta_o)^{[0.88 - 0.88 = 0.00]} = 0.504. \qquad (31)$$

$$\text{For NaCl,} \quad n_{Cl^-} = 0.597\ \ (1.3)^{[0.92 - 0.88 = 0.04]} = 0.604. \qquad (32)$$

$$\text{For LiCl,} \quad n_{Cl^-} = 0.664\ \ (1.4)^{[0.94 - 0.88 = 0.06]} = 0.678. \qquad (33)$$

The values obtained in the transference experiments were: (1) for KCl, 0.505 and 0.505; (2) for NaCl, 0.617 (one result only); (3) for LiCl, 0.694 and 0.699.

Comparison of the two sets of values shows perfect agreement in the case of KCl. In the case of the other two salts the change of the transference number with the change in viscosity is in the right direction but is apparently not large enough. What significance, if any, is to be attached to this difference is a question which must await the accumulation of further experimental data.

The value of the fluidity exponent, m, may, for example, be dependent somewhat upon the nature of the molecules composing the medium through which the ions are moving and although as we have seen above that small changes in m do not greatly affect the calculation of the degree of ionization, they have a much larger influence upon the calculation of the transference number. If, for example, the value of m for LiCl were 0.98 instead of 0.94, this would change the value of γ calculated for a normal LiCl solution at 25°, only from 73.0 to 73.4 per cent. The value for the transference number calculated in equation (33) above, would, however, become 0.687, which is in good agreement with the one obtained by direct measurement.

9. The Viscosity Correction in the Case of Acids and Alkalies.

Johnston found that the relation, $\Lambda = kf^m$, did not hold in the case of hydrogen and hydroxyl ions. If the molecules of water influence the conductance of an acid, or an alkali solution by a kind of Grotthus-

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chain action as suggested by Daneel,[1] then anything which alters the degree of association of the water would influence the magnitude of this effect. In order, therefore, to estimate the degree of ionization of strong acids or alkalies in concentrated solutions, the best procedure would probably be to make use of the equation

$$\gamma = \Lambda/\Lambda'_0 \qquad (34)$$

in which Λ is the equivalent conductance of the solution for which γ is desired, and above which the vapor pressure of the water is p. Λ'_0 is the equivalent conductance of the electrolyte at infinit dilution in a solution to which a suitable non-electrolyte has been added, so as to give it the same viscosity and the same vapor pressure, p, as the first solution. In the absence of any experimental data, however, equation (34) must be regarded merely as a suggestion.

Summary.

1. It is pointed out that in calculating the degree of ionization of an electrolyte by the conductivity method, the neglect of the viscosity effect may produce errors as high as 7 and 8 per cent., even at such low concentrations as 0.1 normal and for such simple electrolytes as uni-univalent salts.

2. The relation $\Lambda = kf^m$ (in which Λ is the equivalent conductance of an ion, f is the fluidity of the solution, m is a constant not far from unity and dependent chiefly upon the nature of the ion, and k is a proportionality constant) is proposed, provisionally as the most logical basis for formulating the viscosity correction in calculating the degree of ionization, γ, in moderately concentrated solutions.

3. The above relation is shown to lead to the following expression for the degree of ionization: $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$. Examples illustrating the results obtained with this equation are given and methods for determining the "fluidity exponent," m, are discussed.

4. The relation $\Lambda = kf^m$ is shown to lead to the following expression for the true transference number n_A of the ion A in any solution: $n_A = n_{0A}(\eta/\eta_0)^{m_A - m}$. n_{0A} is the transference number at infinit dilution in pure water, (η/η_0) the relative viscosity of the solution, and m_A and m are the "fluidity exponents" for the ion and for the salt, respectively. Values calculated from this equation are compared with those determined experimentally.

URBANA, ILL.

THE ACTION OF NITROGEN ON LITHIUM CARBIDE.

BY S. A. TUCKER AND H. R. MOODY.

Received July 1, 1911.

Although particular attention has been given by many investigators

[1] *Z. Elektrochem.*, 11, 249 (1905).

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to the influence of nitrogen on calcium carbide, and the formation of calcium cyanamide, very little work appears to have been done on the action of nitrogen on the carbides *in general*.

Since lithium itself is known to form compounds with nitrogen it seemed desirable to begin a proposed series of investigations with lithium carbide. The investigation is taken up in the following manner:

1. Preparation of Lithium Carbide.
2. Analysis of Lithium Carbide.
3. Preparation of Nitrogen.
4. Absorption of Nitrogen by the Carbide. Method of Carrying on the Experiments, Temperature and Pressure.
5. Analysis of the Product, Total Nitrogen, Condition of Nitrogen in the Product.
6. Experimental Results: Influence of Temperature, Pressure, Time.
7. Conclusions.

1. Preparation of Lithium Carbide.

But little has been published on the preparation of this carbide. Guntz[1] heated metallic lithium and carbon in the air, and in an atmosphere of nitrogen, he also heated the metal in the presence of the gases CO, CO_2, C_2H_2, C_2H_4 and CH_4, and obtained some carbide but none of his experiments gave a pure carbide. His best results were obtained with the metal in an atmosphere of carbon dioxide. Moissan[2] heated lithium carbonate and carbon in his electric furnace, the charge being placed in a carbon tube. The reaction was as follows:

$$Li_2CO_3 + 4C = Li_2C_2 + 3CO.$$

Using 350 amperes at 50 volts seems to have given the best results, and he claims to have obtained nearly pure lithium carbide by this reaction. He noted that with 950 amperes decomposition of the carbide took place at the end of the fourth minute, and observed volatilization of the unchanged carbide, which condensed on the cooler portions of the tube.

The carbide so obtained is described as white with a crystallin fracture. The method followed by the authors for the preparation of this carbide was essentially that of Moissan. A mixture of lithium carbonate and carbon in molecular proportions was heated in three types of electric furnaces: granular-carbon,[3] Borchers[4] and vertical arc.[5]

The first, or granular carbon furnace, gave far the best results, and the preparation was carried out by heating the mixture in a graphite crucible, using from 250–650 amperes at 15–30 volts for from 15 to 17 minutes.

[1] *Compt. rend.*, 123, 1273–5 (1896).
[2] *Ibid.*, 127, 362.
[3] S. A. Tucker, *Trans. Am. Electrochem. Soc.*, 40, 307–15.
[4] Borchers-McMillan, "Electric Smelting and Refining," London, 1904, p. 103.
[5] S. A. Tucker, Vertical Arc Furnaces, *Electrochem. Met. Ind.*, 4, (7) 263.

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On breaking the crucible, the carbide was easily detached from the bottom and sides, and was then analyzed for its content of carbide.

It was soon seen from these experiments that the production of pure lithium carbide was a matter of extreme difficulty, as it was clear that the temperatures of formation and dissociation were close together.

This property is indicated by Moissan's work as well, and it seems to us that to form any considerable mass of pure carbide in this way is practically impossible.

Moissan, as before stated, claims to have obtained nearly pure carbide, but if he did so, it must have been by selecting a small crystal or piece, which gave him the results in accordance with his analysis.

The product obtained by us was for the most part black, and the best results gave a carbide content of 53 per cent. which was obtained with the addition of 4 per cent. of manganese dioxide and a mixture of 60 parts of lithium carbonate and 48 parts of carbon.

The conditions given for the formation of the carbide in a resistance furnace of the granular-carbon type are of course difficult to duplicate on account of the change in the furnace itself. These changes include the variation of the carbon grains, the pressure to which they are subjected, and the number of times the coke has been previously heated in the electric furnace.

After making a number of runs, we were able to judge by the eye alone the right time to withdraw the crucible. When the charge begins to emit fumes of volatilizing metal it is necessary to stop immediately, otherwise the product will be largely contaminated with graphite. This point is also indicated by an apparent rise in temperature, which causes the gases to emit a dazzling white light. Moissan states that lithium carbide is volatil as such. From numerous experiments we have come to the conclusion that this is not the case but that it follows the usual property of the carbides in general of being decomposed by excessive heating into graphite and lithium. It is quite possible that in the dissociation, metallic lithium vapors on coming in contact with a relatively cooled carbon surface form carbide again. Or carbide may be formed by the Guntz reaction as follows:

$$2Li + 2CO = Li_2C_2 + O_2.$$

Either formation of lithium carbide would account for Moissan's belief that he had obtained volatilization of the carbide itself, since he made his preparation in a carbon tube.

The product obtained by the authors was neither uniform nor, as previously stated, pure carbide. Selected masses gave, on analysis, a carbide content of 53 per cent. and these masses were used on the subsequent work on nitrogen absorption. Taking the whole mass it would show a formation not much over 25 per cent. of the theoretical carbide

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yield that could be formed from the proportions of the charge taken.

It is thus seen that the preparation of lithium carbide is attended with difficulty and points to the small temperature interval between its formation and decomposition. Of the carbides studied in other lines of work we have found lithium carbide to possess this property in the most marked degree. The best conditions for preparation, as far as time of heating is concerned, are shown in the following table:

Time.	Amps.	Volts.
11.45	210	18
11.46	250	30
11.49	320	30
11.54	450	30
11.56	650	30
12.00	680	30
12.01	700	30

That is, the heating must be slow and the final high temperature must be of short duration.

With the conditions used by the authors the time of heating could never exceed 17 minutes, the last few minutes being very critical.

Lithium carbide attacks almost any material in which it is heated—porcelain, alundum, graphite and even iron are corroded, the latter withstanding its action best.

2. Analysis of Lithium Carbide.

The value of the product was determined by decomposing with water a known weight of the carbide and noting the loss in weight due to the evolution of acetylene. The operation was carried on in a Rose and Geissler alkalimeter; precautions were taken to decompose the carbide slowly, and the gas as evolved was dried by passing through calcium chloride. Only sufficient water was added to thoroughly decompose the carbide, and towards the end the flask was heated to evolve acetylene which might have been dissolved in the water added.

3. Preparation of Nitrogen.

For the preparation of the nitrogen used in these experiments, molecular proportions of sodium nitrite and ammonium chloride were heated in solution according to the reaction:

$$NaNO_2 + NH_4Cl = N_2 + NaCl + 2H_2O$$

This reaction is best carried out by delivering the nitrite solution from a stop-cock funnel to the solution of ammonium chloride contained in a round bottom Jena flask.

As the reaction is very active the gas is evolved rapidly without additional heating after the reacting temperature is reached. The nitrogen was washed, and then stored in gas holders until required for use.

On analysis the gas was found to contain some oxygen—generally

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from 1 to 2 per cent. As the presence of oxygen is known to be detrimental in the formation of calcium cyanamide from nitrogen and calcium carbide, the gas before using was purified of its admixed oxygen by passing it through a heated tube containing copper gauze. This gave a gas containing less than 0.1 per cent. oxygen by volume and was therefore passed directly into the absorption tube.

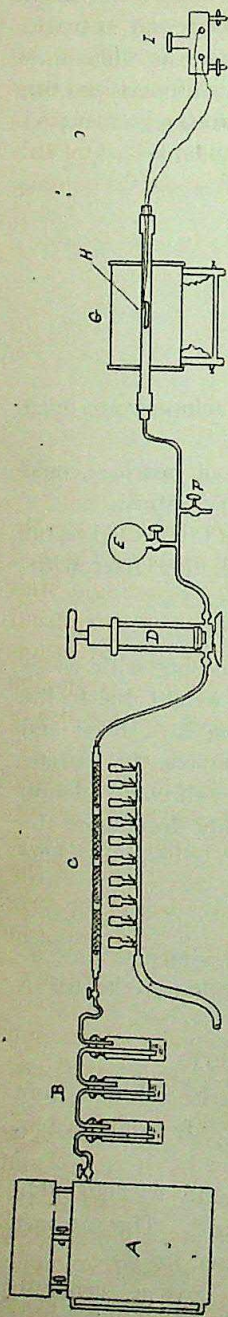

Fig. 1.

4. Absorption of Nitrogen.

As the experimental work involved exposing the heated carbide to the influence of nitrogen at varying pressure and temperature, the arrangement shown in Fig. 1 was adopted.

The first experiments were carried out at atmospheric pressure. Connection was made with the tube of the combustion furnace *C*, containing copper gauze, and the Calorite electric furnace[1] *G*, by means of rubber tubing. The electric furnace *G* was heated to the required temperature and nitrogen passed through the system to displace air.

The carbide in fine powder contained in a porcelain boat holding about 1 gram was then placed in the furnace *G*, at *H*, temperature being read by the thermo-couple at the galvanometer I. Nitrogen was passed slowly through the tube during the time decided upon for the absorption and allowed to escape through a small opening at the end of the tube.

The current was then turned off the electric furnace and the tube was closed with a rubber stopper. The carbide was thus exposed to an atmosphere of nitrogen while cooling.

For use with nitrogen under pressure, the systems *D*, *E*, and *F* were connected, consisting of a force pump *D*, which took nitrogen from the tube in the combustion furnace *C*. An automobil tire pump $1^3/_4''$ diameter was used; this was altered by placing two leathers on the plunger and providing two check valves with brass seats and rubber tips at the bottom.

The gage *E* was an ordinary steam gage, reading

[1] S. A. Tucker, "Electric Furnaces with Calorite Resisters for Laboratory Use", read at May, 1911, Meeting, N. Y. Sec., Am. Chem. Soc.

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to 200 pounds. A needle valve was placed below the gage so that it could be cut out. *F* is another needle valve making connection with a Geryk oil pump to exhaust the air from the system before admitting nitrogen. The carbide contained in a small sheet-iron boat (as iron was found to be least attacked by the carbide) was placed in a special retort, Fig. 2, and connections were made on the pressure side of the system with good quality pressure tubing. Automobil pressure tubing of reinforced rubber is best for this use, as ordinary rubber pressure tubing will blow out at about 40 pounds.

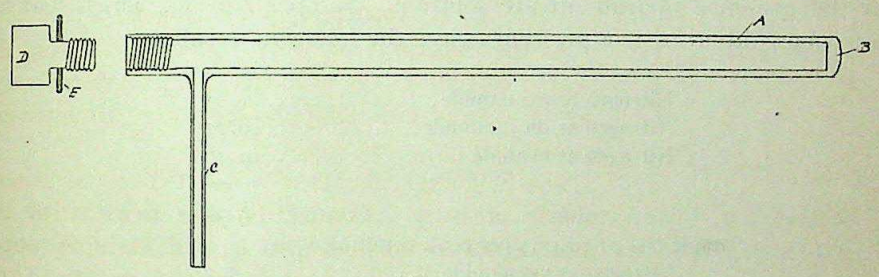

Fig. 2.

The retort shown in Fig. 2 was of cold-rolled steel tubing, 20 cm. long, 18 mm. inside diameter and 25 mm. outside diameter. The end was autogenously welded in the oxyacetylene flame by inserting a steel plug and welding it gas-tight. The other end had a screw thread cut internally and a plug *D* provided, the joint being made gas-tight by means of a standard asbestos copper gasket, *E*. *C* is an iron tube for admission of the nitrogen and is brazed into the tube *A* with copper by the use of the oxyacetylene flame.

The iron boat containing the carbide was pushed to the end of the tube, pressure tubing was connected to *C*, and the system exhausted of air. The retort was then placed in the electric furnace *G*, the temperature adjusted to the required point, *F* was closed, and a few strokes of the pump *D* brought the pressure to 40 pounds. The valve below the gage *E* was now opened and the pressure could be maintained by drawing in nitrogen on the suction stroke of the pump.

5. Analysis of the Product.

After treatment with nitrogen, the product was usually caked and brown, particularly on the surface. It was ground and well mixed and the total nitrogen determined by the Kjeldahl method.

As it was desired, if possible, to determin what compounds of nitrogen existed in the product, a method of analysis adopted by N. Caro[1] and others was used, as follows: 1 gram of the sample was dissolved in 100 cc. of water, made strongly ammoniacal and excess of ammoniacal silver acetate added. The precipitate was filtered, washed free of ammonia

[1] N. Caro, B. Schück and R. Jacoby, *Z. angew. Chem.*, 23, 2405 (1910).

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and the nitrogen determined by the Kjeldahl method. This gives the nitrogen as cyanamide.

For the determination of the dicyanamide, the filtrate was made alkaline with potassium hydroxide, boiled to evolve ammonia and then the nitrogen content of the precipitate, consisting of silver dicyanamide and oxide, determined by the Kjeldahl method.

For nitrogen as cyanide, the method of Feld[1] was used, and consisted in evolving the nitrogen as hydrocyanic acid by distillation of the sample in the presence of lead nitrate solution. Sample No. 40, which had a nitrogen content of 3.18 per cent., gave the following results:

	Per cent.
Nitrogen as cyanamide	1.63
Nitrogen as dicyanamide	0.27
Nitrogen as cyanide	0.18
	2.08

Sample No. 71 = 13.5 per cent. total nitrogen.

Nitrogen as cyanamide	5.2
Nitrogen as dicyanamide	3.4
	8.6

In the latter sample the cyanide was not determined, but it would appear from these results that the product obtained by the action of nitrogen on lithium carbide differs considerably from the corresponding calcium product, or "nitrolime."

Caro gives analyses of "nitrolime" from the Spandau factory which show that nearly all the nitrogen is fixed as cyanamide, with small amounts of dicyanamide and traces of cyanide.

The remaining nitrogen in the authors' product is probably lithium nitride, as this compound is readily produced by the action of nitrogen on metallic lithium and it seems very likely that some metallic lithium would be formed in the preparation of the carbide as carried out in the electric furnace.

6. Experimental Results.

The results obtained are shown in the following tables:

Table I.—Influence of Temperature.

Run No.	Temperature. °C.	Per cent. of nitrogen fixed.	Time Hour.
31	420	0.535	1
32	565	2.25	1
34	715	3.16	1
35	795	3.20	1
36	850	3.36	1
39	925	4.22	1
41	1025	2.64	1

[1] W. Feld, *J. Gasbel.*, 46, [29] 561, [30] 603, [31] 629, [32] 642, [33] 660.

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TABLE II.—INFLUENCE OF TIME.

Run No.	Time. Hour.	Per cent. of nitrogen fixed.	Temperature ° C.
47	1/2	2.92	925
39	1	4.22	925
42 A	2	4.05	925
42 B	3	2.53	925
42 C	4	0.66	925

TABLE III.—INFLUENCE OF PRESSURE.

Run No.	Lbs. sq. inch pressure.	Per cent. of nitrogen fixed.	Time. Hour.
43	35	10.04	1
59	50	16.20	1
71	80	13.5	1

7. Conclusions.

The tables show, first, that more nitrogen is absorbed at a temperature of about 925° than at either higher or lower temperatures; second, that the maximum absorption is reached in one hour and that decreased values are obtained with either longer or shorter periods of heating; and, third, that about 50 pounds per square inch of nitrogen pressure gives the most efficient reaction.

The proportion of nitrogen fixed in the lithium compound does not differ greatly from that obtained commercially with "nitrolime," but the time necessary to so fix it is much less. The nature of the nitrogen compounds formed appears to differ considerably when lithium carbide is used from the compounds obtained when the nitrogen is absorbed in calcium carbide.

So far as the actual quantity of nitrogen so fixed is concerned, much better results might be anticipated with a purer carbide of lithium.

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THE HYDROLYSIS OF IODINE AND OF BROMINE. A CORRECTION.

BY WILLIAM C. BRAY AND E. L. CONNOLLY.

Received July 22, 1911.

The values of the hydrolysis constants $(H^+)(I^-)(HIO)/(I_2) = 0.6 \times 10^{-12}$ and $(H^+)(Br^-)(HBrO)/(Br_2) = 2.4 \times 10^{-8}$, given in a recent article,[1] were calculated from the results of conductance measurements of saturated aqueous solutions of the halogens on the assumptions that $(H^+) = (I^-) = (HIO)$ $[= 4.0 \times 10^{-6}]$ and $(H^+) = (Br^-) = HBrO$ $[= 0.0017]$. Dr. Anton Skrabal, of the Technische Hochschule, Vienna, has kindly

[1] THIS JOURNAL, 32, 932 (1910).

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pointed out by letter that owing to the presence of tri-iodide[1] a smaller value should have been taken for the concentration of iodide ion, and that therefore the value of the constant should be reduced to

$$(H^+)(I^-)(HIO)/(I_2) = 0.3 \times 10^{-12}.$$

On account of a similar neglect of the effect of the presence of tribromide the above value of the hydrolysis constant for bromine is also much too large. According to Jakowkin[2] the "constant" $(KBr)(Br_2)/(KBr_3)$ equals 0.060 to 0.063 in dilute bromide solutions which are one-half to one-tenth saturated with bromine and increases slightly as the concentration of bromine decreases.[3] The results of Boericke[4] and of Worley[5] in more concentrated bromine solutions show, however, that this "constant" decreases rapidly with increasing bromine concentration, and has no significance in saturated solutions. These authors advance the very probable explanation that polybromides higher than the tribromide are present, since the bromide concentration (which is calculated by difference) would then be too small if tribromide is assumed to be the only polybromide present. It therefore seemed improbable that the former conductance measurements in the saturated aqueous solution could be used in calculating the hydrolysis constant of bromine, and the following measurements in more dilute solutions were made.

The experimental methods were exactly the same as in the former investigation. The bromine was purified by shaking with conductivity water until the conductance of the saturated solution was practically the same as that formerly obtained. The dilute bromine solutions were freshly prepared in each experiment, and the concentration of each solution was determined before and after the conductance measurement. The concentration of the hydrogen ion was calculated from the specific conductance by taking, as before, the equivalent conductance of the acid to be 425. This number is probably too large, especially in the more concentrated solutions, since the conductance of the Br_3^- ion is undoubtedly smaller than that of the Br^- ion; but the error is small in the more dilute solutions, where the concentration of HBr exceeds that of HBr_3. Furthermore, the conductance of the hydrogen ion is probably greater than at infinit dilution,[6] which would tend to counterbalance the error due to the presence of tribromide. In the calculations the dissolved bromine which had not undergone hydrolysis was assumed to be present only as

[1] Compare THIS JOURNAL, 32, 924 (1910), Table V.

[2] *Z. physik. Chem.*, 20, 22 (1896).

[3] Compare Jones, *J. Chem. Soc.*, 99, 402 (1911) and Joseph and Jinendradasa, *Ibid.*, 99, 280 (1911).

[4] *Z. Elektrochem.*, 11, 64 (1905).

[5] *J. Chem. Soc.*, 87, 1119 (1905).

[6] THIS JOURNAL, 33, 792 (1911).

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Br_2 and Br_3^-, and the concentration of Br^- was calculated from the relation $(Br^-)(Br_2)/(Br_3^-) = 0.063$.

The results are arranged in the following table in order of increasing bromine concentration. The data in the last line refer to the saturated solution, the conductance and concentration being taken from the former article.

CONDUCTANCE AND HYDROLYSIS OF AQUEOUS BROMINE SOLUTIONS.

Spec. cond. $\times 10^6$.	Concentrations; Formula weights per liter $\times 10^3$. Total Br_2.	$(H^+)=(HBrO)$.	(Br^-).	(Br_3^-).	(Br_2).	$\frac{(H^+)(Br^-)(HBrO)}{(Br_2)}$
261	31.4	0.616	0.415	0.201	30.6	5.2×10^{-9}
291	38.3	0.684	0.429	0.255	37.4	5.4×10^{-9}
287	38.5	0.675	0.423	0.252	37.4	5.2×10^{-9}
398	75.4	0.937	0.431	0.506	74.0	5.1×10^{-9}
503	115.8	1.184	0.422	0.762	113.8	5.2×10^{-9}
506	116.4	1.191	0.422	0.769	114.4	5.2×10^{-9}
545	125.1	1.283	0.434	0.849	123.0	5.8×10^{-9}
549	128.9	1.293	0.430	0.863	126.7	5.7×10^{-9}
727	210.0	1.71	0.40	1.31	207.0	5.7×10^{-9}

An examination of the table shows that the hydrolysis constant is

$$(H^+)(Br^-)(HBrO)/(Br_2) = 5.2 \times 10^{-9}.$$

The results are unexpectedly concordant, but the conductances in the second, seventh and eighth experiments appear to be one or two per cent. too high, and have been rejected, because the chief sources of error would lead to high values.

The increase of the hydrolysis constant with the concentration of bromine is probably due to the presence of a polybromide higher than HBr_3, since this would cause the concentrations (given in the table) of Br^- and Br_3^- in these solutions to be too large but would have practically no effect on the concentration of Br_2. Conversely, by assuming the hydrolysis constant to be 5.2×10^{-9}, the concentration of Br^- in the saturated bromine solution may be calculated. By assuming also that the higher polybromide is HBr_5 the composition of the saturated solution is found to be approximately as follows: Bromide, 0.37×10^{-3}; tribromide, 1.21×10^{-3}; pentabromide, 0.13×10^{-3} (sum, 1.71×10^{-3}); bromine as Br_2, 0.2068.

BOSTON.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE CONSTITUTION OF MARCASITE AND PYRITE.[1]

BY GEORGE W. PLUMMER

Received July 22, 1911.

Attempts have been made at various times to ascertain the state of

[1] For the details of this study consult the author's doctoral thesis, 1910.

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oxidation of the iron in these two minerals. The following experiments were made with the same object in view. In the first efforts equal quantities of the two minerals were exposed to the action of the vapors of carbon tetrachloride at 250° and then at 300°. The results showed that a large percentage of ferrous iron was present in each mineral. On heating weighed portions of the two minerals in sealed tubes at 250° with carbon tetrachloride, the results indicated that about $^3/_4$ of the iron in each mineral remained in the ferrous state. Sulfur monochloride was formed in each case and the inquiry arose as to whether during its formation reduction may not have occurred. It was, therefore, thought advisable to test the action of sulfur monochloride on iron salts. For this purpose 10 cc. of carbon tetrachloride, together with 0.5 cc. of sulfur monochloride and 0.2 gram of dry ferric oxide, were heated under pressure. The ferrous iron content of the ferric oxide had previously been determined by heating with sulfuric acid. It was found that about 2.5 per cent. of the ferric iron was reduced by the sulfur monochloride. Although the reducing action of sulfur monochloride is thus apparent, it is inappreciable in the experiments with marcasite and pyrite, so it may be said it is unlikely that the ferrous iron found in the two minerals was due to the sulfur monochloride. As a result of later work I am inclined to attribute the results obtained in this study of the behavior of carbon tetrachloride with the minerals to the establishment of an equilibrium between the several by-products. While the behavior of carbon tetrachloride is, at least, interesting in itself, it has thrown very little light upon the constitution of marcasite and pyrite.

Upon exposing portions of the two minerals to the action of a 10 per cent. cadmium sulfate solution at a temperature of 250° marcasite was decomposed to the extent of about 35 per cent. and pyrite to nearly 40 per cent. The relative amounts of ferrous and ferric iron were about the same for each mineral but the values were just the reverse of those obtained by the use of carbon tetrachloride, that is, about 20 per cent. of the iron was found to be in the ferrous state and 80 per cent. in the ferric state. It may be remarked that no trace of hydrogen sulfide, sulfurous acid or other reducing agents, nor indeed of any oxidizing agent, could be detected upon opening the tubes in which the experiments were carried out.

When portions of the two minerals were heated with solid ammonium chloride no difference in effect was apparent. The fact that all the iron was found to be in the ferrous state may be attributed to the reducing action of the ammonium sulfide and hydrogen sulfide which were produced.

On heating portions of the two minerals in a sealed tube with arsenic trichloride, little change was effected. Instead of obtaining yellow

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arsenic trisulfide, as was expected, the contents of the tube had a deep blue color when removed from the furnace. After filtering out the insoluble material the filtrate still retained its blue color in reflected light, but in transmitted light it was dark reddish brown. The color was probably occasioned by colloidal arsenic, although it was difficult to verify this, owing to the nature of the solvent in which it was present.

By far the most interesting results of this investigation were obtained by the use of bismuth chloride. An intimate mixture of bismuth chloride and the powdered mineral was placed in a porcelain boat which was then heated in a combustion tube, through which a stream of dry carbon dioxide was passed. It was noticed with marcasite that as soon as the melting point of the bismuth chloride was reached, a reaction occurred. The mass became brown in color, due to the formation of what was supposed to be bismuth sulfide, and upon subsequent treatment of the boat and its contents with water, large quantities of soluble iron were found in the solution, which according to qualitative tests appeared to be almost wholly in the ferrous condition. The gases issuing from the tube, however, contained some hydrogen sulfide, which was detected by passing them through an alkaline lead salt solution. Although the bismuth chloride had been heated to drive out all traces of moisture which it contained, during the operation of weighing the sample and preparing the mixture it must have taken up sufficient to account for the presence of the hydrogen sulfide.

The apparatus was accordingly changed to obviate this difficulty. The form decided upon was very simple. It consisted of a seven-inch test tube supported in an upright position and provided with a doubly perforated cork. A delivery and an exit tube were inserted in the cork, the former extending more than half way down the test tube. About 5 grams of bismuth chloride were placed in the test tube, the mouth being left open, and the salt was then heated until its greenish yellow vapors had mounted nearly to the top of the tube. The Bunsen burner flame was played over the whole of the tube to drive out all the water from the upper portions, and immediately upon removing the flame, the cork was inserted and while cooling, a rapid stream of carbon dioxide was passed through the apparatus. During the time required for cooling, the weighing bottle containing the mineral was tared. When room temperature was reached, the cork was removed for an instant and the quantity of the sample to be tested was dropped carefully down the center of the tube. The cork was replaced and the air which may have entered, again displaced by carbon dioxide while determining the weight of the sample by difference. The tube was then heated, as before, the flame being kept constantly in motion in order to prevent sputtering. Five minutes' fusion was sufficient to decompose both marcasite and pyrite completely. The product was

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allowed to cool in the atmosphere of carbon dioxide and the melt collected in the bottom of the tube in the form of a brown button. This was easily removed when cold and carefully crushed in a mortar to hasten the solution of the iron salts, then dissolved in cold water and washed into a flask of 250 cc. capacity. The tube was also washed several times with water and these washings transferred to the flask, which was subsequently filled to the mark.

By this procedure it was possible to effect the decomposition without the formation of the faintest trace of hydrogen sulfide. The reaction apparently was a simple transposition.

The liquid in the flask contained a precipitate of bismuth oxychloride in addition to the sulfide of bismuth, and in order to determin the iron in solution it was filtered as rapidly as possible through a dry filter and an aliquot part of the filtrate acidulated with sulfuric acid. The ferrous iron was then determined by titrating with potassium permanganate. It was necessary to filter before acidulating, because the quantity of sulfuric acid necessary to add in order to determin the ferrous iron in the presence of the chlorine ions evolved some hydrogen sulfide from the bismuth sulfide when added to the emulsion. The total iron was determined as in the previous experiments, by reducing with zinc and titrating.

The remarkable fact established upon making these titrations was that with both marcasite and pyrite all of the iron was found to be in the ferrous condition. The following table shows the results of some of the determinations made. Over 98 per cent. of the marcasite and over 96 per cent. of the pyrite were decomposed in each of these examples:

RESULTS OBTAINED WITH BISMUTH CHLORIDE.

Mineral.	Weight of sample.	Weight of total iron.	Weight of ferrous iron.
Marcasite	0.2220	0.1014	0.1014
Marcasite	0.3427	0.1579	0.1579
Pyrite	0.2416	0.1072	0.1072
Pyrite	0.2110	0.0955	0.0955

The original solution when acidulated and tested for ferric iron with potassium thiocyanate gave but the faintest pink color, but this may have been occasioned by oxidation during the manipulation.

In order to determin whether the ferrous iron so obtained can be considered as original ferrous iron in the minerals, it was next necessary to determin the quantity of sulfur existing as bismuth sulfide at the completion of the reaction. If all the sulfur were converted by a simple transposition into bismuth sulfide, the amount of hydrogen sulfide liberated from this by the action of hydrochloric acid should contain all the sulfur originally present in the mineral. Accordingly experiments were carried out to determin if such were the case. Since the melt obtained in making

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the fusion, when crushed, did not easily admit of the removal and collection of all the insoluble bismuth sulfide, and since it was not readily disintegrated by water alone, it was placed directly in the generating flask without removing the soluble ferrous chloride. Those parts of the test tube in which the fusion was made, which were coated with any deposit whatever, were likewise broken up and put in the flask with the melt. The sulfur determination was then made according to one of the common methods, *i. e.*, by pouring 1 : 1 hydrochloric acid upon the sulfide and collecting the hydrogen sulfide evolved in ammoniacal hydrogen peroxide. The sulfuric acid was then determined in this solution in the usual way. The results obtained are here appended:

TABLE SHOWING THE AMOUNT OF SULFUR IN MARCASITE AND PYRITE CONVERTED INTO BISMUTH SULFIDE.

Mineral.	Weight of sample.	Weight of total sulfur.	Weight of sulfur in bismuth sulfide.	Pecentage of conversion.
Marcasite	0.1964	0.1045	0.0956	91.4
Marcasite	0.2182	0.1163	0.1060	91.2
Pyrite	0.2162	0.1152	0.1056	91.7
Pyrite	0.2222	0.1184	0.1093	92.4

The extent to which the mineral was decomposed was determined in each of these experiments by titrating the iron in the generating flask with a solution of potassium dichromate, 1 cc. of which was equivalent to 0.0047 gram of iron. Potassium permanganate could not be used for this purpose on account of the large excess of hydrochloric acid present. Complete decomposition had occurred in each case. The quantity of sulfur had already been determined in each mineral, and since the mean of several determinations was very close to the theoretical amount, 53.33 per cent., that value was used in calculating the total sulfur to be expected in the bismuth sulfide.

The fact that some of the sulfur was not in the form of bismuth sulfide, as is shown by a glance at the table, led to a closer study of the reaction, and it was found that some of it was evolved in the form of sulfur monochloride during the fusion. The fact would rather indicate the presence of some free sulfur in the reaction and possibly this may account for the presence of some of the ferrous iron. The 9 per cent. of sulfur, however, which is not converted into bismuth sulfide, would be insufficient to reduce as much as 20 per cent. of the iron present, even if it had an opportunity of acting upon ferric chloride. This is stated conditionally, because it is thought very probable that the sulfur does not reduce any ferric chloride, the reason being that on fusing free sulfur with bismuth chloride, the products obtained are bismuth sulfide and sulfur monochloride. It may be argued from this fact that since the quantity of bismuth chloride is always in large excess, any free sulfur would very likely be taken up by it to form the sulfur monochloride observed,

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simultaneously with, if not before, the formation of the chloride of iron. Hence the conclusion to be drawn as a result of the study of the behavior of marcasite and pyrite with bismuth chloride would be that each mineral contains its iron wholly in the ferrous state. The formula representing them would then have the following configuration: .

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THE USE OF SULFUR MONOCHLORIDE IN THE DETERMINATION AND ANALYSIS OF THE RARE EARTH MINERALS.[1]

BY WILLIAM BROOKS HICKS.

Received July 22, 1911.

Many of the rare earth minerals contain columbium, tantalum and titanium as their acid components. The usual methods of decomposing such minerals are fusion with potassium bisulfate, bifluoride or by treatment with hydrofluoric acid. Each of these methods present difficulties. Fusion with potassium bisulfate is most generally used, but even when one fusion is sufficient to effect the decomposition the resulting mixture containing all the earths is difficult to handle, particularly when a quantitative separation of the metallic acids from the other constituents is desired. On the other hand, the fluoride methods lend themselves to cleaner and more rapid separations but are objectionable because they preclude the use of glass vessels. The present investigation introduces sulfur monochloride as a decomposing agent of such minerals and it is applied in their analysis. Smith,[2] who was the first one to use sulfur monochloride in the decomposition of minerals, showed that many naturally occurring sulfides, as well as rutile, wolframite, scheelite and columbite, were decomposed by this reagent. Oddo and Serra,[3] two Italian chemists, used it in the preparation of anhydrous chlorides of arsenic, antimony and bismuth, while Hall[4] applied it to the preparation of pentachloride of columbium. He also observed that it decomposed such minerals as chromite and columbite and that it converted many oxides into their corresponding chlorides, the notable exceptions being the oxides of boron and silicon. Bourion[5] has used sulfur monochloride in the preparation of anhydrous chlorides in general as well as for the decomposition and analysis of scheelite and wolframite. It, therefore, seemed probable to me that this reagent might decompose such minerals

[1] Details may be found in the author's inaugural thesis, Univ. of Penna., 1911.
[2] THIS JOURNAL, 22, 289 (1898).
[3] *Gaz. chim. ital.*, [2] 29, 355 (1899).
[4] THIS JOURNAL, 26, 1243 (1904).
[5] *Ann. chim. phys.*, 20, 547 (1910).

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as fergusonite, eschynite, etc., with the formation of chlorides. Accordingly they were submitted to its action and the extent of their decomposition carefully noted. The rare earths, after the expulsion of the metallic acids, were examined for scandium. This method of decomposition was also used in the analysis of eschynite. At the outstart, samples of these minerals not altogether pure were used, and while the decomposition was apparently complete, it was felt necessary to submit only the purest material, free from all contamination, to the action of the vapors of sulfur monochloride. The result was that fergusonite was completely decomposed—not a trace of the metallic acids remained in the boat and rare earths could not be detected in the volatil portion. Eschynite was readily and completely decomposed and euxenite yielded without the slightest difficulty to the action of the decomposing agent. A picked sample of samarskite (0.6197 gram) left a residue of 0.0078 gram, which meant a decomposition of 98.78 per cent. All of these minerals, in amounts varying from $^1/_2$–25 grams, were placed in porcelain boats in a combustion tube, which was heated on a furnace while the vapors of sulfur monochloride were passed over them. As previously stated the volatil chlorides of the metallic acids passed into the receiver, while the non-volatil chlorides or oxychlorides of the earth metals remained in the boat.

It was in these non-volatil portions of the minerals that search was made for scandium. In the case of fergusonite, 50 grams of the mineral were decomposed. The boat contents were then dissolved in water and filtered from the gang. Nitric acid was added to the filtrate and the solution evaporated to dryness. The residue was taken up in 800 cc. of 1 : 1 hydrochloric acid and to this boiling solution were added gradually 15 grams of sodium silicofluoride.[1] The boiling was continued for $^1/_2$ hour, when a slowly subsiding and slightly colored precipitate appeared. This was filtered and washed by boiling it with dilute hydrochloric acid. It was then converted into sulfate and the solution treated while boiling with ammonium hydroxide. The resulting precipitate was dissolved in hydrochloric acid and the excess of acid removed by evaporation. The concentrated neutral chloride solution was next added to 50 cc of a 20 per cent. sodium carbonate solution. The white precipitate which appeared at once readily dissolved and on boiling the liquid for half an hour there was no trace of precipitation. This would indicate the absence of scandium. The treatment was repeated several times with different samples of the material with the same negative results or scandium. The substance which had been precipitated from a strongly acid solution with sodium silicofluoride and which failed to give a precipitate on boiling with a 20 per cent. sodium carbonate solution was studied further. For

[1] Meyer, *Z. anorg. Chem.*, 60, 154 (1908).

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example, it yielded a white precipitate with oxalic acid, even in strongly acid solutions. It was completely precipitated by sodium thiosulfate from neutral solution and it showed an atomic weight of 224 on ignition of its sulfate to oxide. Further it was found to be radioactive. These behaviors were taken as conclusive evidence that the substance under examination was thorium, which is not generally mentioned as a constituent of fergusonite, where it evidently exists to the amount of between 2 and 3 per cent.

When the residual chlorides from eschynite were taken up in 1 : 1 hydrochloric acid, and the solution treated with an excess of sodium silicofluoride at the boiling temperature, a copious precipitate appeared. It was washed with dilute hydrochloric acid, converted into the sulfate and then back into the chloride. The latter when treated with sodium carbonate yielded a white precipitate after a few minutes' boiling. This precipitate was filtered, washed several times with a sodium carbonate solution, then with water, after which it was dissolved in hydrochloric acid and precipitated with ammonium hydroxide and reprecipitated in order to get rid of the last traces of sodium. 100 grams of the mineral were decomposed and the chloride solution precipitated twice with sodium silicofluoride, once with sodium carbonate and once with oxalic acid. The oxalate was ignited to oxide and weighed 0.0320 gram equivalent to 0.03 per cent. of the mineral. The fact that a precipitate was produced by sodium carbonate was pretty strong indication that eschynite contained scandium, but to test this point farther the spark spectrum of the chloride was studied. A Rowland grating was used and the second order spectrum photographed as a standard of comparison. The iron spectrum was photographed on one-half of the plate and also served as a means of detecting the air lines, because these would show in both halves of the plate. The photographs were made of the portion of the spectrum which contained the strongest scandium lines, that is, from 3,500–5,000, measured in Angstrom units. The wave lengths were then measured by projecting the lines on a screen, containing an accurately divided scale, from such a distance that the wave lengths of different known iron lines would fall on the proper scale divisions. When this was done, the wave lengths sought could be read directly. As a result of this study no scandium lines were detected. There were few strong lines, leaving out those of platinum, but a larger number of dim lines. In general, the latter corresponded very closely to the lines of yttrium and thorium, though it must be stated that some of the stronger yttrium and thorium lines were not noticed. The conclusion is that the substance which had been separated from eschynite by sodium silicofluoride and sodium carbonate was not scandium but a mixture of yttrium and thorium. A

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similar experiment was conducted with euxenite with like result and scandium was not observed in samarskite.

For the analysis of eschynite some pure crystals, as free as possible from foreign matter, were ground to a fine powder, and then subjected to the action of sulfur monochloride. As the decomposition proceeded, the volatil chlorides and the excess of sulfur monochloride passed into a dilute nitric acid solution and were there decomposed. Much of the sulfur was oxidized and consequently, less free sulfur was precipitated. At the end of the operation, dry hydrochloric acid gas was passed through the combustion tube, and, by means of a free flame, all the volatil portion was driven out. After cooling in a current of hydrochloric acid gas, the tube was cut by scratching with a file and touching with a hot glass rod. The short end of the tube and the glass cover were thoroughly washed into the beaker, which now contained all the columbium, tantalum, titanium, tungsten and most of the iron from the mineral as well as a considerable amount of separated sulfur. This mixture was treated as follows:

The lumps of sulfur were broken up as much as possible by means of a glass rod, a large excess of ammonium hydroxide was added, and then hydrogen sulfide in sufficient quantity to dissolve the sulfur completely. The yellow ammonium sulfide, thus formed, dissolved the tungstic acid, leaving the acid earths and iron in the residue. This was filtered off. By acidifying the filtrate, tungsten sulfide was precipitated along with a large amount of sulfur. After filtering, the precipitate was washed with water, alcohol and carbon disulfide. The precipitate was then evaporated with nitric acid, ignited, and weighed as WO_3.

The residue, containing iron and the acid earths, was digested with hot, dilute sulfuric acid until perfectly white. All the iron and some of the acid earths went into solution, which was decanted through a filter, and the residue washed. Hydrogen sulfide was passed into the filtrate to reduce the iron, and then sodium carbonate was added until the solution became almost neutral. This solution was boiled for an hour, during which time a current of hydrogen sulfide was passed through the solution to prevent the oxidation of the iron. By this means, the acid earths were completely precipitated, while the iron was left in solution. This precipitate was added to that obtained above, ignited, and weighed. No attempt was made to separate columbium, tantalum and titanium.

The non-volatil portion was dissolved in water, to which a few drops of hydrochloric acid had been added. The solution was boiled, and filtered from the gang. The filtrate was treated with hydrogen sulfide to remove the lead and tin. These were separated in the usual way. The filtrate, after removing the lead and tin, was treated with an excess of

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ammonium chloride and ammonium hydroxide. All the iron and rare earths were precipitated. Calcium was determined in the filtrate. The rare earths were separated from the almost negligible amount of iron by ammonium carbonate and ammonium sulfide.

By an application of this method of procedure, the following results were obtained:

	Per cent.
Cb_2O_5, Ta_2O_5, TiO_2	53.55
ThO_2, Ce_2O_3, La_2O_3, Y_2O_3, etc.	41.30
WO_3	0.17
SnO_2	0.04
FeO	0.82
CaO	0.55
PbO	0.91
Gang	0.22
Loss on ignition	2.25
	99.81

The only purpose of this analysis was to show that the sulfur monochloride method of decomposition could be used in the analysis of eschynite. The results obtained above prove this point. Owing to the lack of time neither columbium, tantalum, and titanium, nor the rare earths were separated, yet it is obvious that any of the methods proposed for separating these elements could readily be applied.

The principal advantages of this method are the readiness with which the mineral is decomposed by sulfur monochloride, the simplicity and cheapness of the apparatus required, and the separation of columbium, tantalum, titanium and tungsten from the rare earths during the decomposition. The chief disadvantage that has been encountered in applying the method is the treatment of the volatil portion which consists of the excess of sulfur monochloride mixed with the volatil chlorides. This has been successfully dealt with by allowing the mixture to pass into dilute nitric acid and then removing the precipitated sulfur by adding excess of ammonium hydroxide and hydrogen sulfide.

Since fergusonite, euxenite, and samarskite are completely decomposed by sulfur monochloride with the separation of columbium, tantalum, titanium and tungsten from silica and the rare earths, it is evident that this method of decomposition could, likewise, be used in their analysis. By analogy, we would reason that columbates, tantalates, and titanates in general would be decomposed by sulfur monochloride, and that this method of decomposition would lend itself to their analysis.

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THE ATOMIC WEIGHT OF TANTALUM.

BY WILLIAM H. CHAPIN AND EDGAR F. SMITH.

Received July 22, 1911.

I. Introduction.

It is scarcely necessary to mention the older work of H. Rose and Marignac, not by any means because it lacks importance, but because it is so well known. The values for tantalum that stood upon our lists of atomic weights for many years were worked out by these men, especially the latter.

The value now standing upon the table is 181. This was determined by F. Willy Hinrichsen and N. Sahlbom by oxidation of metallic tantalum to the pentoxide. Their series contains five determinations, having among them an extreme variation of 1.2 units, the lowest value being 180.59 and the highest 181.77.

There has recently been published in THIS JOURNAL, **32**, 1117, an article on the "Atomic Weight of Tantalum" by C. W. Balke. He determined the constant by transposing pure tantalum pentachloride into the oxide.[1] His method of preparing the pure materials was extremely good, as was also the process of conversion into oxide. The mean of his series of eight very concordant values is 181.52.

A year ago an attempt was made in this laboratory by W. K. Van-Haagen to determin the atomic weight of tantalum by transposing the pentabromide into oxide. Difficulties experienced in getting this compound in a pure condition made the values high and discordant; but it was nevertheless thought to be possible to overcome these difficulties, and with this in mind the present investigation was undertaken.

II. Preparation of Pure Materials.

Tantalum Oxide.—It is scarcely necessary to give an extended description of the methods employed in preparing pure tantalum oxide. They were such as have been used over and over again in this laboratory, and have been proved to be perfectly reliable. The starting-out material was potassium fluotantalate. This was six times recrystallized with centrifugal drainage. The reagents used were carefully purified, and nothing ever came in contact with the salt but hard rubber and platinum.

The oxide was obtained from this fluotantalate by treatment with the best obtainable sulfuric acid, subsequent hydrolysis, and washing. The last traces of water were finally removed by long extended ignition.

Special care was taken throughout this investigation to exclude dust.

Bromine.—The bromine was purified by dissolving in calcium bromide solution, and then distilling in apparatus constructed entirely of glass.

[1] *Proc. Am. Phil. Soc.*, **43**, 143.

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This process removed every objectionable substance, including chlorine, of course. A possible trace of iodine would not be removed, but it has already been shown in this laboratory that tantalum iodide cannot be produced by combination with the oxide, and even if it were possible, it could not exist in presence of an excess of bromine.

At the time of the first distillation an excess of potassium permanganate was added to decompose any hydrobromic acid, and to remove water the product was shaken with concentrated sulfuric acid, and subsequently redistilled.

Carbon.—The method of preparing the pentabromide called for the bromination of the oxide in presence of pure sugar carbon. It had been found very difficult, if not impossible, to prepare sugar carbon absolutely free from traces of hydrocarbons, which upon bromination would of course cause the production of hydrobromic acid. Van Haagen believed that it was the presence of this that indirectly caused the high value. His theory was that some compound analogous to the columbium compound, Cb_2O_5xHCl was formed. With this in mind, special care was taken to remove hydrocarbons, the carbon being placed in a large porcelain crucible packed in charcoal in a Hessian crucible, and heated in a furnace until, upon removal, the cover of the porcelain crucible was found to be fused on. A combustion of this carbon, however, showed the presence of about 0.02 per cent. of hydrogen, and a second heating did not reduce the amount. A further attempt to remove the last traces of hydrogen consisted in the bromination of the carbon in a Jena tube at a high temperature. Even this treatment served only to slightly lower the percentage.

To prove the truth or fallacy of Van Haagen's theory, tantalum oxide was heated in an atmosphere of hydrogen bromide for an hour. The result was entirely negative. However, the presence of hydrogen would certainly insure the formation of a trace of water during the bromination of the oxide, and this would as certainly cause the decomposition of a corresponding amount of the pentabromide. Just what the product would be was not known at the time, but it was thought that it might be an oxybromide, $TaOBr_3$, although the authorities denied the possibility of producing an oxybromide of tantalum. Considering, then, the seeming impossibility of removing the last traces of hydrogen from the carbon, it looked as if the only alternative was to prepare the bromide with possibly a slight uncertainty as to its composition, and then rely upon methods of fractional distillation for obtaining an absolutely pure product.

Concerning the carbon, it remains only to be said that 20 grams, when burned completely in a porcelain crucible, left no ponderable residue.

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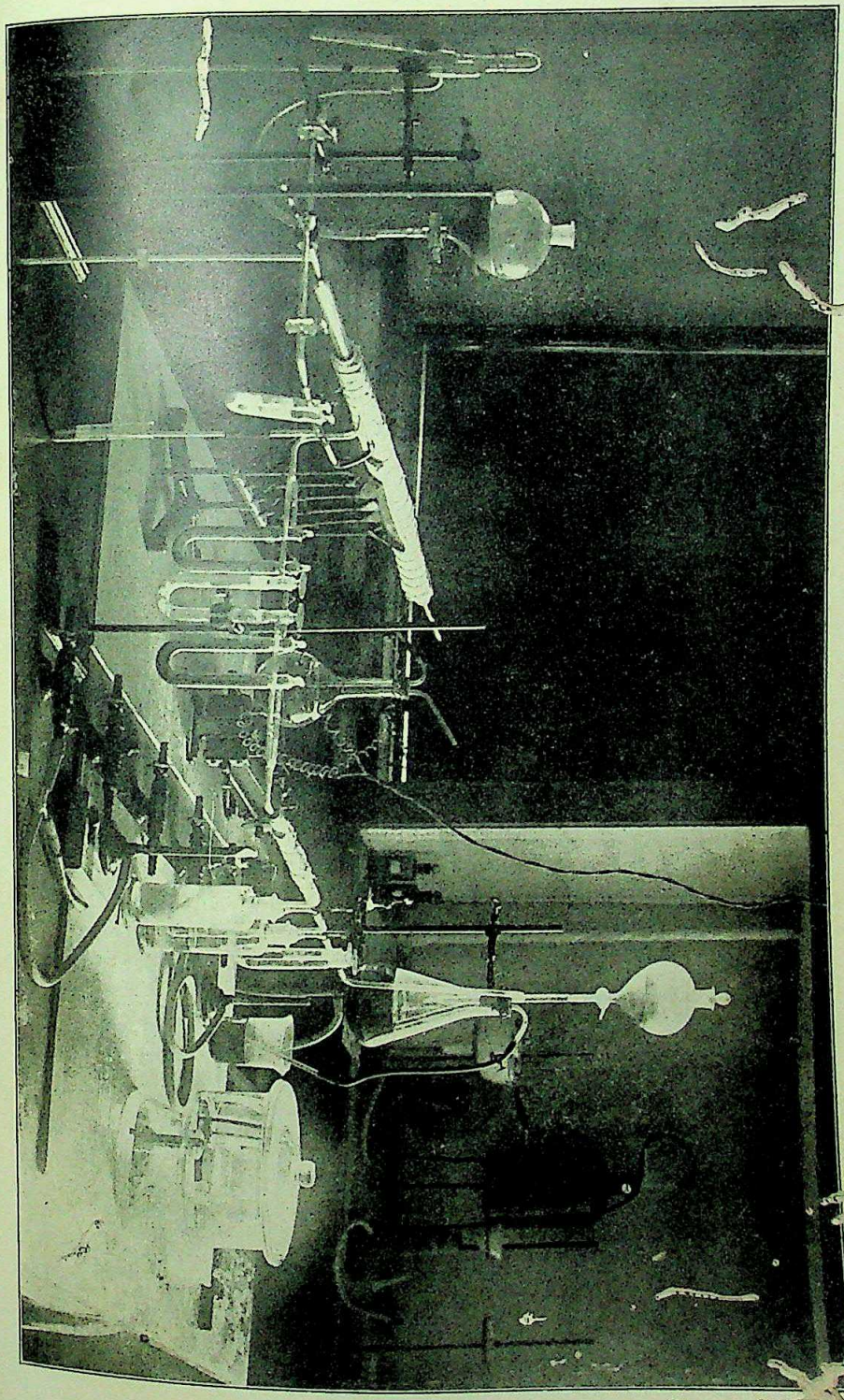

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I. I. Preparation of the Pure Bromide.

Bromination of the Oxide.—The method of preparing a bromide by conducting bromine vapors over a red-hot mixture of an oxide and sugar carbon is familiar to almost every one. It needs only to be said that special care was taken in this case in the construction of the apparatus. All parts which were to come in contact with bromine were made entirely of glass, either sealed together or connected by ground joints. The bromine was carried by a current of carbon dioxide, special care being exercized to obtain this pure and absolutely dry. The cut of apparatus used later in the fractional distillation shows very well the arrangement of the parts used in this case. The carbon dioxide, after passing through sodium bicarbonate to remove traces of hydrochloric acid, and through sulfuric acid to remove water, passed next over a red-hot copper spiral to remove any oxygen, and then to the system of U-tubes seen in the foreground. Here the course was divided, the gas passing either through the bromine tube, and then a phosphorus pentoxide tube, or through the latter tube alone. This arrangement made it possible to clear the tube of air and subsequently of bromine with perfectly dry carbon dioxide. This gas was generated by action of dilute hydrochloric acid on marble. It scarcely needs mentioning that the latter was boiled under reduced pressure to remove air. The generator was so arranged that the spent liquid could be withdrawn without opening. In fact it was kept in operation for more than a month without the admission of any air. All the acid used was boiled and was transferred to the tap-funnel without contact with air. It was subsequently kept entirely in an atmosphere of carbon dioxide.

Distillation of the Pentabromide.—By the above-mentioned method about 100 grams of the pentabromide were prepared. The only possible impurity that this could have contained was some compound of tantalum related to the pentabromide but containing an excess of oxide, and the distillation was conducted with the intent of removing this. It had previously been noticed that when the crude product was redistilled a much less volatil residue remained, and it was hoped that a few distillations would completely remove this. The apparatus used for the first distillations consisted simply of a Jena tube having two constrictions near one end. The charge (about 50 grams) was placed in the tube and a rapid current of carbon dioxide conducted for some time to remove air. Heat was then applied; when at a temperature of about 250° the salt melted, and immediately began to distil away, condensing beyond the constriction in beautiful dark red laminae. After completing one distillation the heating apparatus was shifted, and the bromide distilled beyond the next constriction. Finally, after completing the distillation, the salt was melted down and allowed to cool to a hard mass.

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When entirely cool this contracted away from the glass, and could easily be dropped out in a single piece directly into a large weighing tube standing in a desiccator. Four distillations made after this manner left the bromide most beautiful in appearance, but the tube was not left entirely clean. A slight film of yellowish color was still seen adhering to the glass. At a high temperature, however, this was somewhat volatil, and it was therefore uncertain whether the separation was complete. A trial determination of the atomic weight made with this material gave the value 187.00, hence it did not seem probable that the maximum of purity had been reached.

It was thought that if the bromide could be distilled a number of times without removal from the tube the desired end might be attained. For this purpose a Jena tube seven feet long having six constrictions was prepared, and the distillation conducted with this as before. The result was disappointing, for even the sixth distillation left the same yellowish film on the glass—thinner than before, perhaps, but distinctly visible. A trial determination of the atomic weight made at this point gave the value 182.70—only a slight improvement over the first value.

With another tube of similar construction six more distillations were conducted, part of them in an atmosphere of bromine, but there was no apparent improvement, a slight film being left after each distillation. Two trial determinations made here gave the values 182.28 and 182.32, indicating homogeneity of material, and something of a change in composition. However, it scarcely seemed as if pure material could ever be obtained by this method if sixteen distillations had apparently failed to give it. It was thought that possibly the carbon dioxide still contained traces of air (oxygen), or that the carbon dioxide itself brought about a slight decomposition of the bromide. At any rate it was decided to carry out the process of distillation in a vacuum.

Sublimation in Vacuo : The Oxybromide.—The apparatus used for the vacuum distillation is shown in the cut. The distilling tube was connected on the one hand with a mercury pump, which gave a vacuum of 1 mm., and on the other with a carbon dioxide or nitrogen generator, an arrangement which permitted the alternate evacuation and filling of the tube. This was necessary, since it was found best to use a tube with several constrictions as before, and to seal off after each distillation so as to preclude the possibility of contaminating the pure material by an after-distillation of the separated impurity. The heating was accomplished by means of a resistance coil of "nicrome" ribbon. This was wound upon a glass jacket, and so arranged that one end of the tube could be heated to 300° while the other remained at about 200°. The jacket was made movable, and during a distillation was pushed over the inner tube step by step until the temperature was just sufficient to distil the

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pentabromide and leave the impurity behind. It should be noted here that in a complete vacuum the former does not melt but simply sublimes.

The tube seen in the cut extending downwards from the end of the combustion tube dips into a tube of mercury, and acts as a manometer. The stopcocks on either side were lubricated with a mixture of rubber and paraffin, making them absolutely air-tight. The rubber stopper at the end of the combustion tube was covered, after insertion, with several coats of lacquer. After evacuation the apparatus was always left for some time to be absolutely sure that there was no leakage, the manometer reading being compared with that of a barometer standing near by.

This method of fractionation did not always work out smoothly, but in general the results were very good. Using a tube with three constrictions, and sealing off after each distillation, the amounts of residue were about like those shown in the following example:

Weight of $TaBr_5$	12.0 grams
Residue after first distillation	0.19 gram
Per cent	1.58 per cent.
Residue after second distillation	0.0064 gram
Per cent	0.053 per cent.
Residue after third distillation	trace

Considering these facts, it was believed that the pentabromide obtained by distillation *in vacuo* was pure. Trial determinations on different samples prepared in this manner gave values for the atomic weight ranging from 181.7 to 181.9.

The nature of the yellow residue: As has been suggested, it seemed quite probable that, in spite of statements to the contrary, an oxybromide of tantalum did exist, and that this residue was that very compound. As obtained in these distillations, it was an extremely light, feathery substance, very deceptive in its appearance, leading one to believe that there was a much greater quantity than really existed. One analysis conducted on a very small sample gave the following results:

Substance taken	0.0628 gram
Oxide obtained from this	0.0323 gram
Per cent	51.4

Allowing 182 as the atomic weight of tantalum, the oxybromide, $TaOBr_3$, would give of oxide 50.7 per cent. Therefore, considering the smallness of the sample, the agreement seemed as close as could be expected, and there was left little reason to doubt that this was really a true oxybromide of tantalum.

IV. Determination of the Atomic Weight.

The method of determining the atomic weight through the pentabromide is rather simple. This salt, like the chloride, is instantly decom-

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posed by water, halogen acid being given off and the metallic base being left behind in the form of the white hydrated oxide. The latter, upon strong ignition, goes to the pentoxide, Ta_2O_5. To bring about complete expulsion of bromine, nitric acid must be used in small amounts, this being added after the greater part of the hydrobromic acid has been evaporated off.

From the above it is very evident that up to the time when the pentabromide has been weighed out it must be kept absolutely out of contact with every trace of moisture. Indeed this fact constitutes the most difficult problem connected with the preparation and preservation of this substance. As has already been indicated, the pentabromide, after distillation and subsequent cooling, contracted sufficiently to separate itself from the walls of the combustion tube, and could therefore be dropped out in a single piece. If the container was placed in a large desiccator under phosphorus pentoxide, there was very little chance for decomposition. This, in fact, was the method pursued, and to make a safe transference of the bromide the end of the combustion tube was simply placed within the mouth of this container and then tilted until the piece slid out, or if necessary was pushed out with a glass rod. To further prevent any contact with moist air, the stopper of the container was very slightly lubricated with paraffin, and held in place by means of a rubber band. The piece of pentabromide as obtained usually weighed from 12 to 20 grams, and could easily be broken up into pieces of convenient size by tapping with a long glass rod, a process which required only a partial removal of the desiccator cover, and certainly could not have allowed any moisture to reach the salt. It might be stated here that the proof of this statement was seen later, when, upon running a series of four determinations and thus opening the tube four different times, the last of the series gave the lowest result, which would not have been the case had an appreciable amount of moisture reached the tube.

The weighing out of the sample of pentabromide for analysis was conducted in the following manner: A glass weighing tube was used whose stopper fitted over the outside of the neck. This prevented soiling at the time of emptying out the sample, and consequent trouble about getting the stopper back. This weighing tube was placed open in the desiccator beside the tube containing the pentabromide, and in its mouth was placed a wide short-stemmed funnel. At the same time the rubber band about the bromide tube was removed and the stopper slightly loosened. The cover of the desiccator was then replaced and left for half an hour, until every trace of moisture should be removed from the weighing tube. Next the desiccator was partially uncovered, and by means of a pair of long glass forceps a single piece of the pentabromide was quickly transferred to the weighing tube, the funnel removed, and

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the stopper dropped in place. Great care was taken not to push the latter on, since the contained air could thus be slightly compressed and would remain so. It was allowed to settle down slowly by its own weight, and finally gently tapped into place.

Having thus made the transference, the weighing tube was placed upon the balance pan and allowed to remain there for fifteen minutes, at the end of which time it was weighed. (The balance was one of Troemner's best make, and the weights were carefully calibrated.) After the weight was taken the sample was carefully dropped out into a weighed porcelain crucible, the latter standing inside a larger crucible of the same kind, and the tube was then reweighed. The greatest care was always taken to touch the tube as little as possible, and also to allow a sufficient time for readjustment after such contact. In the case of the crucibles a counterpoise of almost exactly the same size and weight was used. In applying the vacuum correction the value 4.67 was taken as the density of the pentabromide. This had previously been determined by Van Haagen. The correction amounted to 0.00013 gram for each gram of substance taken.

The crucible containing the pentabromide was placed on a water bath and about half filled with pure distilled water. With a solid piece of the pure pentabromide there was never any tendency to spatter or hiss. In fact the piece usually remained perfectly bright and apparently unaffected for several minutes after the water was applied. It should be noted here that the water bath was constructed entirely of porcelain, and only distilled water was ever used in it.

When the sample had finally become completely hydrolyzed the water and acid were evaporated off. To remove the last traces of bromine the oxide was at this point covered with pure 10 per cent. nitric acid, and the evaporation repeated.

The crucible was next placed within a porcelain air bath, and with cover in place was heated cautiously until the oxide became apparently dry, and all the nitric acid was expelled.

The final step was the strong ignition, which was conducted first over a Bunsen burner and then over a good blast lamp. The blasting was, of course, repeated until constant weight had been reached, and usually required about forty-five minutes.

In weighing the oxide no vacuum correction was applied since the density of tantalum oxide is not far from that of the brass weights. In calculating the atomic weight the value 79.92 was taken for bromine; that of oxygen was 16, of course. The following table contains the results of all determinations which were carried through to completion and were not known to be in error:

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Wt. of $TaBr_5$. (vac.).	Wt. of Ta_2O_5. (vac.).	Ratio $TaBr_5 : Ta_2O_5$.	At. wt. of Ta.
0.86837	0.33117	2.6221	181.68
1.50903	0.57570	2.6212	181.80
1.56554	0.59718	2.6216	181.75
1.23239	0.47030	2.6204	181.91
1.31815	0.50295	2.6208	181.85
1.31702	0.50244	2.6212	181.80
1.20090	0.45830	2.6204	181.91
1.04050	0.39688	2.6217	181.74
		Mean,	181.80

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ACTION OF HYDROFLUORIC ACID GAS UPON CERTAIN OXIDES.

BY WALTER K. VAN HAAGEN AND EDGAR F. SMITH.

Received July 22, 1911.

From time to time in this laboratory various metallic oxides have been exposed at varying temperatures to the influence of gaseous halogen acids. In the past summer we have taken occasion to ascertain the volatility or non-volatility of certain oxides when heated in hydrofluoric acid gas. The latter was generated from well dried calcium fluoride and concentrated sulfuric acid contained in a platinum retort which was connected with a platinum combustion tube, in which there was also a platinum boat carrying the material to be acted upon. The constricted portion of the combustion tube was cooled by means of a moist wad of filter paper, while its extreme end was allowed to dip into distilled water. The retort and its contents were gradually heated in a glycerol bath, by which means a constant and even flow of hydrofluoric acid gas was obtained.

On treating strongly ignited and powdered aluminium oxide as above indicated, the boat and its contents became exceedingly hot to the touch but there was no volatilization of the material. At a white heat a small portion of fluoride of aluminium could be detected in the receiver. The conversion of oxide into fluoride was perfectly quantitative after heating in the bath for twenty minutes.

Yttrium oxide suffered a complete change at a red heat to fluoride or oxyfluoride. There was no volatilization and, therefore, no yttrium was found in the receiver.

The conversion of lanthanum oxide to fluoride was also quantitative and there was no volatilization of lanthanum salt. Finely divided quartz volatilized easily and completely without the application of external heat. The heat of the reaction was intense.

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In the action of titanium oxide volatilization took place below a red heat and was complete at this temperature.

Zirconium oxide was fully converted at a red heat into fluoride, a portion of it passing into the receiver but the greater part remaining in the constricted portion of the water-cooled part of the combustion tube in crystallized form. The boat was empty.

Finely powdered zircon mineral when heated to a dull red heat sustained complete decomposition. Zirconium was found in the receiver liquid. Nothing was left in the boat. The major portion of the zirconium lodged in the constricted part of the tube in large crystals, which dissolved almost wholly in water, but complete solution required the addition of a few drops of hydrochloric acid.

Cerium dioxide quantitatively changed to fluoride without any volatilization.

Thorium dioxide suffered a slight alteration without any volatilization.

Tin stone was converted only slightly into a fluoride or oxyfluoride, which was volatilized with extreme difficulty at a white heat.

Columbium and tantalum pentoxides were completely expelled from the boat in which they were present at a low red heat.

The volatilization of tantalum fluoride proceeded with more difficulty than in the case of columbium fluoride.

On exposing one-half gram of powdered columbite to the action of hydrofluoric acid gas, the mineral was completely decomposed. The columbic and tantalic oxides which were expelled and caught in the receiver amounted to 78 per cent. A careful analysis of the mineral previously made showed 80 per cent. of these mixed oxides. The boat contained a fused residue consisting of iron and manganese. This dissolved in water, although a few drops of dilute hydrochloric acid were added to produce a clear solution.

The mineral fergusonite was similarly decomposed with a complete volatilization of the metallic acids, while the contents in the boat consisted of fluorides of rare earths, *e. g.*, yttrium, lanthanum, etc.

The following salts were treated in a similar manner: (*a*) Potassium dichromate lost nearly all of its chromic acid by this treatment. (*b*) Sodium tungstate was attacked with difficulty and the tungstic acid was not completely expelled. (*c*) Sodium pyrophosphate in a finely divided state was attacked at the ordinary temperature with evolution of a great amount of heat. The phosphoric acid was completely driven into the receiver. The residue in the boat was soluble in water and gave no precipitation when its solution was treated with silver nitrate. An example will show how complete this change was: 0.4794 gram of sodium pyrophosphate left a residue weighing 0.3026 gram instead of the calculated 0.3028 gram. Indeed, the change was effected with so much ease

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and was of such a truly quantitative character that it was thought that the atomic weight of phosphorus might readily be determined in this way. This investigation is now in progress. It will give the ratio of P : NaF. As sodium fluoride is readily converted into sodium chloride the ratio of P : NaCl is the one that is being determined. Incidentally, this will also give the ratio of F : Cl.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ACTION OF SALICYLIC ACID UPON THE METALLIC ACIDS.[1]

BY JOHN HUGHES MULLER.

Received July 22, 1911.

On exposing the hydrates of columbium, tantalum and titanium to the action of a number of organic acids salicylic acid alone showed a marked difference in its behavior with them. An excess of salicylic acid was slowly added to a solution of sodium columbate and a precipitate, gelatinous in form and orange-yellow in color resulted. Continued digestion of this precipitate at boiling temperature caused it to become bright yellow in color and to lose much of its gelatinous form. After washing with water containing some salicylic acid to prevent hydrolysis, the precipitate was dried and the percentage of columbium present determined by the ignition of weighed quantities, thus converting them to columbic oxide. The precipitation of the columbium was complete.

On precipitating an alkaline tantalate solution with salicylic acid the precipitate, while gelatinous, was colorless. This reaction was also quantitative.

Warm solutions of ammonium hydroxide and potassium hydroxide decompose these salicylates of columbium and tantalum. They are insoluble in ether, methyl alcohol, ethyl acetate, chloroform, carbon tetrachloride, carbon bisulfide, and petroleum ether.

The presence of an alkali fluoride prevents the precipitation of columbium or tantalum by salicylic acid. Orthotitanic acid dissolves in salicylic acid in the presence of fluorides to an almost colorless solution and in their absence to an intensely yellow colored salicylate. Zirconium and thorium hydroxides are difficultly soluble in aqueous salicylic acid while after ignition the corresponding oxides are practically insoluble.

Known amounts of each of the oxides of columbium, tantalum, zirconium and thorium were mixed with weighed amounts of titanic oxide and these mixtures then fused with 5 grams of potassium carbonate, the fusions being taken up in from 350–400 cc. of water at 60° and treated with 14–15 grams of salicylic acid, the solution being heated for three to

[1] From the author's Ph.D. thesis.

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four hours at the boiling temperature. The precipitates were allowed to settle, filtered rapidly and washed with boiling water. The concentrated filtrates were treated with ammonium hydroxide, when the titanium was precipitated, washed and ignited to oxide. These precipitates were invariably contaminated with alkali salicylates which could not be removed by washing. They were therefore fused with potassium bisulfate and the corresponding oxides obtained in the usual manner.

TITANIC OXIDE AND COLUMBIC OXIDE.

Cb_2O_5 taken.	Cb_2O_5 found.	TiO_2 taken.	TiO_2 found.	Number of fusions.
0.3042	0.3047	0.2989	0.2989	3
0.3080	0.3075	0.3204	0.3204	3
0.3489	0.3486	0.0200	0.0187	2
0.3040	0.3046	0.0530	0.0530	3
0.3001	0.3005	0.0020	0.0019	2
0.2980	0.2981	0.0011	0.0012	1
0.3022	0.3025	0.0063	0.0060	2
0.4000	0.4000	0.0006	0.0006	1

TITANIC OXIDE AND TANTALIC OXIDE.

Ta_2O_5 taken.	Ta_2O_5 found.	TiO_2 taken.	TiO_2 found.	Number of fusions.
0.3050	0.3054	0.4010	0.4015	4
0.3019	0.3021	0.1020	0.1021	3
0.5020	0.5021	0.0006	0.0006	1
0.3046	0.3051	0.0515	0.0512	2
0.5020	..	0.0153	0.0155	2
0.5040	0.5048	0.0005	0.0005	1

TITANIC OXIDE AND THORIUM OXIDE.

ThO_2 taken.	ThO_2 found.	TiO_2 taken.	TiO_2 found.	Number of fusions.
0.4998	0.4997	0.1030	0.1035	2
0.0590	0.0595	0.3027	0.3026	3
0.9658	0.9658	0.0020	0.0019	1
0.7377	0.7380	0.0027	0.0025	1
0.9658	0.9659	0.0005	0.0006	1
0.7380	0.7380	0.0009	0.0010	1

TITANIC OXIDE AND ZIRCONIUM OXIDE.

ZrO_2 taken.	ZrO_2 found.	TiO_2 taken.	TiO_2 found.	Number of fusions.
0.3035	0.3024	0.3016	0.3030	2
0.0996	0.0990	0.5000	0.4991	3
0.0726	0.0715	0.5719	0.5730	3
0.4481	0.4472	0.0047	0.0050	2

The intense color produced by the addition of salicylic acid to alkaline titanates suggested a colorimetric determination of this metal, while the characteristic nature of the reaction pointed to its possible estimation in the presence of oxides, none of which produce a marked coloration with the same acid.

A 0.5000 gram portion of titanic oxide was fused with 5 grams of potas-

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sium carbonate, the melt taken up in warm water and treated with an excess of salicylic acid. Refusion of the small residue and repetition of the process brought all the oxide into solution. The combined solutions were diluted to exactly 500 cc. at 20–23°. 100 cc. of this intensely colored solution were removed and diluted to 1 liter, which latter volume then contained 0.1 gram of titanium dioxide and still exhibited an intense yellow color inclining to orange. A set of standards was prepared by dilution of known volumes of this stock solution, carrying out the dilution as far as practicable, noting the intensity and permanence of the color reaction as compared to the quantity of oxide present.

Grams of TiO_2 per 100 cc. . . .	0.1	0.01	0.005	0.0025	0.0010
Color of solution.	Orange-red	Orange	Deep yellow	Bright yellow	Yellow
Grams of TiO_2 per 100 cc. . . .	0.0005	0.00025	. . .	0.0001	0.00005
Color of solution.	Light yellow	Sulfur-yellow	. . .	Pale yellow	Faint yellow

The solutions were kept in 100 cc. Nessler tubes (2 cm. in diameter). The last two faded considerably on standing for several days, but the addition of a little aqueous salicylic acid was found to render the more dilute solutions just as permanent in color as those of greater concentration. Standing for one month with no special precautions, other than exclusion of dust, caused no appreciable change in color intensity. Blanks, containing sodium salicylate and salicylic acid which had been boiled for several hours, were compared with the highest dilution, *i. e.*, 0.00005 gram TiO_2 per 100 cc. A distinct difference was still observable. Two other sets of standards were now made, using double the amount of alkaline flux in one case, and double the excess of salicylic acid in the other. No difference in color intensity could be found, the three sets being exactly similar in appearance. Very small amounts of hydrofluoric acid or fluorides interfered with the delicacy of the reaction. Appreciable quantities absolutely destroyed the yellow color. Traces of iron interfered, producing the familiar purple color used in the detection of this acid and other phenolic compounds. The presence of zirconium gave a brownish cast to the solutions, sufficiently deep to make a determination of titanium in the presence of this oxide quite impossible. Columbic oxide interfered. Tantalic oxide did not seriously affect the results, although tending to give high results for titanium.

Alkaline molybdates gave a yellow color closely resembling that caused by a titanate. The oxides of thorium, tantalum, lanthanum, cerium and yttrium did not cause the slightest interference in the colorimetric determination. Small quantities of neodymium, praseodymium, and a mixture of erbium and terbium oxides did not give a color with salicylic acid; larger amounts developed colors that obscured the yellow.

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Experiments with small quantities of columbic oxide (0.002–0.002) gave colorless filtrates, after precipitating in the usual way with salicylic acid. This is additional evidence that dissolved columbic oxide was not the cause of the brownish color imparted to the filtrates from the columbium determinations. The author cannot repress the conviction that an unknown substance, only noticeable in large amounts of the columbic oxide, was the cause of the brownish color. In the following tables titanium was determined colorimetrically, while the columbic and tantalic oxides were estimated by difference.

TITANIC OXIDE AND COLUMBIC OXIDE.

Cb_2O_5 taken.	TiO_2 taken.	Cb_2O_5 found.	TiO_2 found.	Number of fusions.
0.3025	0.1000	0.3045	0.0980	3
0.3110	0.0105	0.3102	0.0113	2
0.5032	0.0010	0.5028	0.0019	1
0.0101	0.0500	0.0091	0.0510	2
0.0050	0.0005	0.0048	0.0007	1

TITANIC OXIDE AND TANTALIC OXIDE.

Ta_2O_5 taken.	TiO_2 taken.	Ta_2O_5 found.	TiO_2 found.	Number of fusions.
0.3105	0.0205	0.3103	0.0207	2
0.4439	0.0020	0.4441	0.0018	1
0.5050	0.0005	0.5049	0.0006	1
0.3000	0.0005	0.3000	0.0005	1
0.0502	0.0010	0.0499	0.0011	1

TITANIC OXIDE AND THORIUM OXIDE.

ThO_2 taken.	TiO_2 taken.	ThO_2 found.	TiO_2 found.	Number of fusions.
1.0020	0.0500	1.0010	0.0510	3
0.5001	0.0206	0.5002	0.0205	2
0.8763	0.0010	0.8759	0.0014	1
1.0002	0.0008	0.9999	0.0011	1

The results for titanium in the presence of columbium are high. To correct these errors the solutions were heated to boiling, and the color due to titanium discharged by the addition of ammonia, again comparing the residual color with the standards. The brownish solutions were, however, not comparable with the pure yellow of the standards, and in consequence the colorimetric estimation of titanium in this mixture had to be given up.

On the other hand, tantalic oxide did not interfere, enabling a very rapid determination of small quantities of titanic oxide without the necessity of the ammonium hydroxide precipitation.

The results with thorium were high, probably because of the large amounts of thorium or traces of impurity in the oxide.

This colorimetric method is evidently of little practical value, owing to the interference of the common contaminants of titanic oxide. It

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may, however, be conveniently used for the very accurate determination of nearly pure titanic oxide, and especially for the detection of this oxide in the acid earths. As a test for titanium in the absence of molybdenum and iron, the delicacy of the reaction considerably exceeds any reaction for this metal with which the writer is acquainted. As little as 0.00005 gram of titanic oxide in 100 cc. shows a pale yellow, while 0.0001 gram in the same volume produces a very marked and permanent sulfur-yellow color. In the presence of large quantities of columbium or zirconium the brownish yellow color produced might be mistaken for the yellow of titanium, but this yellow color of titanium solutions is immediately discharged by ammonia, while the brownish yellow color due to columbium or zirconium is permanent in alkaline solution, and only appreciable when a large quantity of the last-mentioned metals are present.

Ten grams of sodium tungstate dissolved in 200 cc. of water gave no precipitate with salicylic acid. Ten grams of sodium molybdate, containing 66.66 per cent. MoO_3, were treated in the same manner as the tungstate. The behavior was almost the same as that of the tungstate. The solution, however, was deep yellow, while a lighter colored very similar amorphous substance separated when the solution was concentrated to a small volume (25–30 cc.).

The tungsten and molybdenum solutions failed to give a precipitate with ammonium hydroxide while the alkaline solutions remained colorless. The above reactions seemed to indicate a possible separation of these two metals from titanium by precipitation of the salicylic acid solution with ammonium hydroxide. Likewise the solubility of the molybdate and tungstate in salicylic acid suggested the removal of columbic and tantalic oxides from molybdenum and tungsten.

Molybdic oxide in large quantity completely prevented the precipitation of columbium by salicylic acid. The attempt to separate titanium from both tungsten and molybdenum, by this method, gave incomplete precipitation and turbid filtrates, which could not be cleared by a second or third filtration.

The separation of tungsten and columbium was more satisfactory, giving values not far from quantitative, requiring for success, however, a relatively small amount of tungsten.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

AN EMPIRICAL RELATION BETWEEN THE CONFIGURATION AND ROTATION OF SUGARS.

BY ERNEST ANDERSON.

Received May 15, 1911.

It has long been known that some sugars rotate polarized light very

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strongly while other closely related sugars rotate this light but slightly. No satisfactory explanation of this fact has ever been given.

Recently, while comparing the configurations and rotations of the various sugars, I noticed that the configuration of the α and β carbon atoms seems to determin the direction and degree of optical rotation of the sugars. It is possible, in fact, to decide from a glance at the configuration of these carbon atoms, approximately what the rotation of a sugar will be.

There are four possible configurations for the α and β carbon atoms in sugars. These configurations with their corresponding rotations are:

```
      OH  H
1. —C—C—C—X;[1] dextro, strongly.[2]
      H  OH ||
            O

      H   OH
2. —C—C—C—X; levo, strongly.[2]
      OH H  ||
            O

      OH OH
3. —C—C—C—X; dextro or levo, slightly.[3]
      H  H  ||
            O

      H   H
4. —C—C—C—X; dextro or levo, slightly.[3]
      OH OH ||
            O
```

Sugars having any one of the above groups rotate as indicated. The following table shows that this statement is true for all sugars for which both configuration and rotation are known.[4]

TABLE I.

Sugar.	Configuration.	Specific rotation.
d-Glucose	H H OH H CH_2OH—C—C—C—C—CHO OH OH H OH	+52°.5
d-Galactose	H OH OH H CH_2OH—C—C—C—C—CHO OH H H OH	+83°
l-Arabinose	OH OH H CH_2OH—C—C—C—CHO H H OH	+105°

[1] X may be H or CH_2OH.
[2] More than 20°.
[3] Less than 20°.
[4] The data in all the tables of this paper have been taken from: Maquenne, *Les Sucres et Principaux Derives*; Lippmann, *Chemie der Zuckerarten*; Fischer, *Untersuchungen über Kohlenhydrate und Fermente*; and from the articles by Hudson, THIS JOURNAL, 32, 338; 33, 405.

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TABLE I (*Continued*).

Sugar.	Configuration	Specific rotation.
l-Xylose	H OH H CH_2OH—C—C—C—CHO OH H OH	+20°
Rhodeose	OH OH H CH_3—CHOH—C—C—C—CHO H H OH	+86°
d-Fructose	H H OH CH_2OH—C—C—C—C—CH_2OH OH OH H ‖ O	—92°
Isorhamnose	OH OH H OH CH_3—C—C—C—C—CHO H H OH H	—30°
d-Sorbose	OH H OH CH_2OH—C—C—C—C—CH_2OH H OH H ‖ O	—43°
α-Rhamnohexose	OH OH H H OH CH_3—C—C—C—C—C—CHO H H OH OH H	—61°.4
Fucose	H H OH CH_3—CHOH—C—C—C—CHO OH OH H	—77°
d-Mannose	H H OH OH CH_2OH—C—C—C—C—CHO OH OH H H	+14°
l-Rhamnose	OH OH H H CH_3—C—C—C—C—CHO H H OH OH	+9°
d-Tagatose	H OH OH CH_2OH—C—C—C—C—CH_2OH OH H H ‖ O	+1°
α-Glucoheptose	H H OH H H CH_2OH—C—C—C—C—C—CHO OH OH H OH OH	—19°.7
d-Lyxose	H OH OH CH_2OH—C—C—C—CHO OH H H	—14°
l-Gulose	H OH H H CH_2OH—C—C—C—C—CHO OH H OH OH	—(slightly)

The above-described relation between configuration and rotation makes possible the determination of the unknown configuration of some sugars. For this purpose it is necessary to know the specific rotation

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of the sugar whose configuration is unknown and the configuration of the sugar from which the sugar of unknown configuration was synthesized.

As an illustration, the configuration of α-glucooctose: The configuration of α-glucoheptose is, $CH_2OH.\overset{H}{\underset{OH}{C}}.\overset{H}{\underset{OH}{C}}.\overset{OH}{\underset{H}{C}}.\overset{H}{\underset{OH}{C}}.\overset{H}{\underset{OH}{C}}.CHO$. The α-hydroxyl in this sugar becomes the β-hydroxyl in α-glucooctose. The specific rotation of α-glucooctose is −50.5° and, hence, it must have the configuration $-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-CHO$ about the α and β carbon atoms and must therefore be,

$$CH_2OH-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-CHO.$$

Table II contains four groups of sugars in each of which the configuration of the first member is known and the configurations of the succeeding members are obtained as indicated for α-glucooctose.

TABLE II.

Sugar.	Specific rotation.	Configuration.
		Group 1.
α*d*-Glucoheptose	−19°.7	$CH_2OH-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-CHO$
α*d*-Glucooctose	−50°.5	$CH_2OH-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-CHO$
Gluconono se	+ (slightly)	$CH_2OH-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-CHO$
		Group 2.
d-Mannose	+14°	$CH_2OH-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-CHO$
d-Mannoheptose	+85°	$CH_2OH-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-CHO$
d-Mannooctose	−3°.3	$CH_2OH-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-CHO$
		Group 3.
d-Galactose	+83°	$CH_2OH-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-CHO$

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TABLE II (*Continued*).

Sugar.	Specific rotation.	Configuration.
α-Galaheptose	—(slightly)	H OH OH H H CH_2OH—C—C—C—C—C—CHO OH H H OH OH
β*d*-Galaheptose	—54°.4	H H OH H OH CH_2OH—C—C—C—C—C—CHO OH OH H OH H
Galaoctose (from α-Galaheptose)	—40°	H OH OH H H OH CH_2OH—C—C—C—C—C—C—CHO OH H H OH OH H
	Group 4.	
α-Rhamnohexose	—61°.4	OH OH H H OH CH_3—C—C—C—C—C—CHO H H OH OH H
α-Rhamnoheptose	+8°.4	OH OH H H OH OH CH_3—C—C—C—C—C—C—CHO H H OH OH H H

The above table establishes the configurations of eight sugars, which up to the present were only partially known.

The relation between configuration and rotation makes possible the prediction of unknown rotations of sugars whose configurations are known. Table III contains five such sugars.

TABLE III.

Sugar.	Configuration.	Predicted rotation.
l-Ribose	OH OH OH CH_2OH—C—C—C—CHO H H H	± (slightly)
d-Talose	H OH OH OH CH_2OH—C—C—C—C—CHO OH H H H	± (slightly)
β-Rhamnohexose	OH OH H H H CH_3—C—C—C—C—C—CHO H H OH OH OH	± (slightly)
d-Idose	OH H OH H CH_2OH—C—C—C—C—CHO H OH H OH	+ (strongly)
β-Glucoheptose	H H OH H OH CH_2OH—C—C—C—C—C—CHO OH OH H OH H	—(strongly)

There is a very simple theoretical explanation of the above described relation between configuration and rotation but this will not be presented until the evidence has been completed.

CHICAGO, ILL.

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SOME NEW SOLVENTS FOR CELLULOSE AND THEIR ACTION ON THIS SUBSTANCE.[1]

By Horace G. Deming.

Received June 20, 1911.

Introductory.

No simple solvent is known for the so-called normal cellulose, of which the cotton fibre is the type. It is precipitated from solution in a modified form,[2] and its esters appear to be not derivatives of normal cellulose, but of hydrocelluloses whose nature has not been determined.[3] The reagents which dissolve cellulose may be classified as follows:

1. Certain solutions of metallic salts in the presence of acids. Zinc chloride in aqueous solution (where some free acid is always present because of hydrolysis) and the same salt in hydrochloric acid solution appear to be the only examples recorded.

2. Certain organic reaction mixtures, in which the cellulose dissolves with the production of esters.

3. Ammoniacal solutions of copper hydroxide, copper carbonate, and cuprous chloride,[4] and solutions of copper hydroxide in the alkylamines.[5]

4. Certain strong mineral acids. Concentrated sulfuric acid, phosphoric acid, and nitric acid (sp. gr. 1.52) were previously known to dissolve cellulose.

This paper will present some new solvents under several of the above heads, with some of the data which have been obtained regarding esterification and hydrolysis of cellulose in such solutions.

The material employed in all cases was an excellent filter paper, such as is used for quantitative determinations (Schleicher and Schüll, No. 595). It contained 0.095 per cent. ash, and its hygroscopic moisture, determined by drying at 110°, was 5.13 per cent. The material contained a little oxycellulose, as was shown by its reducing power with Fehling's solution. Thus 100 grams of material reduced 0.95, 1.18, average 1.05 grams of copper (calculated). The copper reduced in this and in all succeeding experiments was determined by electrolysis from a 10 per cent. sulfuric acid solution, in which the cuprous oxide formed had been dissolved.

Action of Metallic Salts in the Presence of Acids.

A concentrated aqueous solution of zinc chloride dissolves cellulose when warmed slightly. The first stage of the reaction is a swelling of

[1] I wish to extend thanks for valuable advice and directions to Professor Louis Kahlenberg, at whose suggestion this work was undertaken.

[2] Schwalbe, "Die Chemie der Cellulose," p. 145.

[3] Ost, *Z. angew. Chem.*, 19, 995 (1906); Häussermann, *Z. Schiess u. Sprengwesen*, 3, 305.

[4] Rosenfeld, *Ber.*, 12, 956 (1879).

[5] *Z. angew. Chem.*, 19, 497 (1906).

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the fiber, probably accompanied by hydration, as cellulose which has been previously hydrated by the mercerizing process dissolves in the reagent with unusual ease.[1] The next step in the act of solution is a further modification of the cellulose by the acid, which is always present from the partial hydrolysis of the salt. The following facts support this conclusion:

1. Cellulose dissolves in a solution of zinc chloride in concentrated hydrochloric acid with much greater ease than in a solution of the same salt in water.[2]

2. Hydrocelluloses, produced by the action of dilute acids on cellulose, dissolve in the solution in water to a greater extent than do unaltered celluloses at the same temperature. Rough experiments show that more than half of the hydrocellulose prepared according to Girard[3] is soluble in a cold aqueous solution of zinc chloride at 20°, while less than 10 per cent. of an unaltered cellulose is dissolved in the same time. Hydrocellulose prepared in this way is, however, a mixture of substances, some of which are quite insoluble in the cold reagent.

3. Liquids which dissolve zinc chloride without liberating hydrochloric acid by hydrolysis are unable to dissolve cellulose. The salt for example dissolves readily in pyridine and quinoline, but such solutions do not dissolve cellulose, even at the boiling temperature. Certain celluloses which have been altered by dilute acids are, however, soluble in these reagents. Zinc chloride dissolves to a considerable extent in acetone, ethyl acetate and lactic acid, but such solutions do not dissolve unaltered cellulose. No experiments have been made on the solubility of the altered celluloses in these reagents.

After showing the necessity for the presence of free acid, it seemed likely that solutions of other salts of a weak base and a strong acid might dissolve cellulose in aqueous solution, or at least in solution in concentrated hydrochloric acid. Many such cases were found, and are recorded below.

Water added in small quantities to crystals of antimony trichloride produces a clear solution, which dissolves cellulose in the cold, and more quickly on warming. A solution of the same salt in aniline does not dissolve cellulose even on boiling, but one in concentrated hydrochloric acid effects solution in the cold.

Strong solutions of mercuric chloride and bismuth chloride in concentrated hydrochloric acid make splendid solvents for cellulose even in the cold. Four parts of stannous chloride dissolved in one part of water

[1] Ger. Pat., 11886, 118837.
[2] *Chem. Ztg.*, 18, 441 (1894); *Chem. News*, 63, 66 (1891).
[3] *Ann. chim. phys.*, [5] 24, 350 (1881).

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bring cellulose into solution when warmed to 100°, while the same salt in concentrated hydrochloric acid is effective in the cold.

Antimony pentachloride, tin tetrachloride, and titanium tetrachloride mixed with a small amount of hydrochloric acid dissolve cellulose. In the case of the last mentioned solution one can best observe the fact that the cellulose fibers swell up and become transparent before dissolving.

Cobalt chloride, auric chloride, uranyl chloride, cerous chloride, and chromic chloride are less efficient. To secure a clear solution in such cases it is necessary to filter the liquid through an asbestos felt which has been washed with concentrated hydrochloric acid, as portions of the fibers remain undissolved. Aqueous hydrochloric acid solutions of cadmium chloride, cuprous chloride, thallic chloride and vanadium chloride are relatively poor solvents, but all dissolve some cellulose. Manganous chloride, cupric chloride and nickel chloride were employed in the form of the hydrated salts, which were dissolved in concentrated hydrochloric acid. In each case they are without action. Silver chloride, lead chloride, thallous chloride, thoric chloride, aluminum chloride, phosphorus chloride, and arsenic trichloride all fail to dissolve cellulose in acid solution. These results are possibly due, in some cases, to the fact that the salt is but poorly soluble in the concentrated acid. Zirconium chloride in concentrated hydrochloric acid solution dissolves but little cellulose, except at high temperatures where the organic material is so far decomposed as no longer to permit of recovery by dilution with water.

The action of bromides in acid solution is complicated by the fact that hydrobromic acid has such a powerful effect on cellulose. The decomposition of the latter by hydrobromic acid gas in ethereal solution, with the production of brommethylfurfural, is well known.[1] A concentrated aqueous solution of hydrobromic acid dissolves cellulose almost instantly with profound decomposition, but the following observations were nevertheless made. Aqueous zinc bromide dissolves cellulose, but zinc fluoride is but slightly soluble and so fails to act. Bismuth bromide and mercuric bromide dissolved in hydrochloric acid dissolve cellulose at concentrations where an equivalent amount of hydrobromic acid would disintegrate the fibers without dissolving them. The same is true of the iodides of zinc and mercury in hydrochloric acid solutions, which dissolve cellulose readily. Lead iodide and bismuth iodide dissolved in hydriodic acid dissolve cellulose, but the concentrated acid itself has considerable solvent power.

Neutral solutions of the halogen salts of the alkalies and alkaline earths are unable to effect solution, but what has been said would lead one to expect some of these solutions to dissolve cellulose which has been previously altered by the action of acids. This is actually the case, and a

[1] Fenton and Gostling, *J. Chem. Soc.*, 79, 361, 807 (1901).

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subsequent report will deal with the action of such reagents on various modified celluloses. As an example may be mentioned the fact that a solution of calcium chloride boiling at 130° will at that temperature dissolve the modified cellulose precipitated from the formic-hydrochloric acid reagent described later. The hydrocellulose of Girard is soluble in the calcium chloride solution to a large extent at the same temperature.

The chlorides of the alkalies and alkaline earths do not dissolve cellulose in hydrochloric acid, perhaps on account of the fact that the salts are but sparingly soluble in the acid. One might expect to find that solutions of these salts in other acids would dissolve cellulose. In fact solutions of calcium chloride, calcium bromide, barium chloride, magnesium bromide, lithium chloride and potassium bromide in formic acid, or in mixtures of the latter with hydrochloric acid do dissolve cellulose. A similar but less decided action is obtained with solutions of lithium chloride and calcium chloride in trichloracetic acid.

Precipitation takes place when solutions of cellulose in any of the above reagents are poured into water, but the action is often not complete until after several days. The product must be entirely free from acid if it is to possess stability. Washing is best effected by separating the precipitate in a centrifuge, shaking it up with water and separating again. After several such operations a few drops of normal alkali will render the wash-water neutral. Final separation is made on a Büchner funnel.

The dried product is an extremely hard, hornlike mass, almost colorless if prepared with care, and resembling the cellulose recovered from solution in Schweizer's reagent. The yield from solution in antimony trichloride dissolved in concentrated aqueous hydrochloric acid at room temperature was about 60 per cent. of the weight of the original material, when the product was precipitated by dilute acids within one hour from the time of solution. The air-dried sample contained 10.0 per cent. moisture, determined by drying in the air at 105°. It also contained 0.40 per cent. ash, and was easily soluble in concentrated hydrochloric acid, partly soluble in cold 10 per cent. sodium hydroxide solution, and very slowly soluble in Schweizer's solution. Its reducing power was determined as directed by Schwalbe,[1] except that a smaller sample was weighed out and boiled with 150 cc. of Fehling's solution. A 0.4040 g. sample gave 0.0716 g. copper, corresponding to a copper number of 20.8, corrected for moisture and ash.

The rate of hydrolysis of the cellulose appears to vary with the nature of the salt which has aided in effecting its solution. The action proceeds to a stage where the material can no longer be precipitated by water, and results in the production of considerable glucose, as shown by the osazone test. The absence of large quantities of dextrins among the final products

[1] *Z. angew. Chem.*, 23, 924 (1910).

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of the cellulose hydrolysis is indicated by the low rotatory power of the solutions. For example, 0.80 g. cotton, dried at 110° and dissolved in a solution of 25 g. pure antimony trichloride and concentrated hydrochloric acid, showed a rotation of +0.83° in a 1 dcm. tube, after making up to 50 cc. with the concentrated acid and allowing to stand for 17 hours before polarizing. $[\alpha]_D = 51.9°$.

Some results were obtained regarding the hydrolysis of cellulose in other reagents mentioned above, but no discussion or quantitative description will be attempted until the work is complete.

Esterification and Hydrolysis in Formic Acid Solution.

Details for the esterification of cellulose in the presence of different condensing agents will be found in the recent text-books of Schwalbe[1] and Piest.[2] Cellulose formates prepared with the use of sulfuric acid as a catalyzer were studied by Woodbridge.[3] Recent patents call for the use of zinc chloride[4] or gaseous hydrochloric acid,[5] but the products of the reaction have not been investigated.

A cellulose ester was prepared by the solution of 3.0 g. of filter paper in 100 cc. of formic acid which had been saturated at room temperature with dry hydrochloric acid gas. The product precipitated after four hours was slowly soluble in formic acid, slightly soluble in pyridine, and insoluble in the other reagents which dissolve the different cellulose acetates. If allowed to remain in the acid liquid for 24 hours before precipitating, the ester thus formed is saponified, yielding a modified cellulose identical with that obtained from the mixture of hydrochloric acid, formic acid, and calcium chloride described below.

When calcium chloride is substituted for the hydrochloric acid gas the cellulose is esterified, and a portion is dissolved. The calcium chloride probably aids the esterification by bringing the cellulose into solution in the way previously noted. The amount of cellulose dissolved by this method is, nevertheless, small.

The dissolved ester is precipitated by the addition of alcohol or water, but the reaction mixture may be diluted with concentrated hydrochloric acid without causing a precipitate to form. This observation suggests the use of a mixture of hydrochloric acid, formic acid, and calcium chloride to dissolve cellulose. The product recovered from such a solution is not an ester, but a modified cellulose produced by the saponification of an ester by the mineral acid.

It may be mentioned that a mixture of 30 cc. of formic acid (sp. gr.

[1] "Die Chemie der Cellulose," Berlin, 1910.
[2] "Die Cellulose," Stuttgart, 1910.
[3] THIS JOURNAL, 31, 1067 (1910).
[4] U. S. Pat. 655,082; Ger Pat. 219,163.
[5] Ger. Pat. 189,837.

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1.22), 70 cc. hydrochloric acid (sp. gr. 1.40), and 10 g. calcium chloride will dissolve 1.5 g. of cellulose within fifteen minutes, while a mixture of the two acids alone will effect no solution in twenty-four hours. Addition of as little as four grams of calcium chloride to the acid mixture will cause almost complete solution within half an hour. We may conclude that there is some specific action of the metallic salt, since the addition of an equivalent amount of hydrochoric acid gas does not bring about solution.

In order to investigate the modified cellulose recovered from the solution in this reagent, 25 cc. of concentrated hydrochloric acid were mixed with 25 cc. of formic acid and 5 grams of calcium chloride. About 2.5 g. filter paper dissolved in the liquid to a clear syrup in about one hour. The material was precipitated with water, washed with the aid of a centrifuge, and dried for several weeks in a vacuum at room temperature over sulfuric acid.

Analysis by combustion gave the following figures:

Calculated for $(C_6H_{10}O_5)_6.H_2O$: C, 43.63; H, 6.26.
Ash, 0.37%. Found: C, 43.42, 43.50; H, 6.05, 5.93.

Material dried in this way evidently contains a slight excess of water over that contained in normal cellulose.

A second sample was prepared in the same way as before, except that the material was allowed to remain dissolved in the acid mixture for three hours before precipitating. The acid-free sample was dried in an air oven at 110° for three hours, when its weight was practically constant. Analysis by combustion gave:

Calculated for $C_6H_{10}O_5$: C, 44.44; H, 6.17.
Ash, 0.55%. Found: C, 44.19, 44.00; H, 6.17, 6.24.

Ost[1] found the figures 44.26 and 6.25 for cotton cellulose, from which we may conclude that the modified cellulose under consideration has the same percentage composition as the former, or differs from it by an amount too small to be detected by elementary analysis.

The modified cellulose prepared as described above is slowly soluble in Schweizer's reagent and in concentrated hydrochloric acid if freshly precipitated. On drying, it becomes insoluble in cold concentrated hydrochloric acid, and dissolves in Schweizer's reagent only on standing for a number of days. About 45 per cent of the material will dissolve in cold 10 per cent. sodium hydroxide solution in three days. It is not permanently stained with iodine unless first moistened with sulfuric acid, when it receives a deep blue color. It is soluble in the acid solvents for normal cellulose, but is distinguished from the latter by its marked reducing power and ready hydrolysis.

[1] *Z. angew. Chem.*, 19, 993 (1906).

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No. 1. 1.5189 g. substance gave 0.1256 g. copper. Corrected copper number 20.6. No. 2. 0.4443 g. substance gave 0.1862 g. copper. 0.6137 g. substance gave 0.2533 g. copper. Corrected copper number 42.88, 42.46. No. 3. 0.2154 g. substance gave 0.0296 g. copper. 0.2154 g. substance gave 0.0256 g. copper. Corrected copper number 12.1, 10.2.

Sample No. 1 had remained in the acid liquid for two hours before being precipitated. It had been mixed with silica to aid washing, and contained 59.93 per cent. ash and 2.12 per cent. moisture, determined at 110.°.

Sample No. 2 had been in solution for 36 hours, in a mixture of 100 cc. of formic acid (sp. gr. 1.22), 100 cc. water, 300 cc. of hydrochloric acid (sp. gr. 1.20), and 50 g. anhydrous calcium chloride. It contained 0.27 per cent. ash and 3.94 per cent. moisture.

Sample No. 3 had been in solution two hours. Its reducing power was determined approximately by pipetting off 50 cc. of an acid-free suspension of freshly precipitated material. The total weight of the solid matter was determined in another sample of 50 cc. The ash content was 30 per cent.

The correction for the copper solution absorbed by the filter paper used in separating the cuprous oxide was taken as 0.0037 g. in all determinations. It is evident that the reducing power of the material under consideration is increased by long contact with the acid solvent, or even by drying in the air.

To compare the rate of hydrolysis of normal cellulose with that recovered from solution in the reagent under study, samples were weighed out and boiled for four hours with normal hydrochloric acid, the reducing power of the filtrate being determined with the following results: 3.1291 g. S & S paper No. 595 gave 0.5133 g. copper; 0.4285 g. modified cellulose, 0.4346 g. copper. This corresponds to a hydrolysis of about 8 per cent of the filter paper, as compared with 50 per cent. of the modified cellulose.

From what has been stated it is evident that a solution of cellulose will be rapidly hydrolyzed by the strong acid present. Samples which have not been diluted with water are no longer precipitated by water after twenty-four hours. Only about 80 per cent. of the material can be recovered, even if precipitation takes place within one hour.

We may conclude that dextrins of high rotation are absent from the first products of hydrolysis, because the substances not precipitated by water show a very low optical activity. For example, with 10.2 g. dry filter paper, about 7.9 g. were precipitated by water after being in solution for about one hour. The filtrate was concentrated under 35 mm. pressure, and most of the calcium removed by sulfuric acid. After diluting with water and concentrating again under diminished pressure,

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a solution was obtained which showed a rotation of +0.37° in a 2 dcm. tube, after the volume had been made up to 200 cc. This is about one-third of the rotation which would be produced by an equal amount of glucose.

Longer action of the strong acid solution results in the production of considerable amounts of glucose. A solution of eight grams of filter paper after four days produced no precipitate when poured into water. The greater part of the calcium chloride and acid was removed as described above, then the solution was neutralized with sodium carbonate and allowed to evaporate at room temperature to a moist cake. This was treated with absolute alcohol to precipitate the remaining salts, which were extracted several times with boiling 95 per cent. alcohol. After the removal of the alcohol the product was fermented with compressed yeast in a current of purified hydrogen. The carbon dioxide evolved weighed 1.120 grams, this being a yield of about 30 per cent. fermentable sugar, calculated as glucose. Glucose was isolated in large quantities as the osazone (m. p. 204° to 206°) and as the pentabenzoate (m. p. 179° after crystallization from alcohol). A fermentation experiment was successful when carried out without first removing the inorganic salts by means of alcohol, but the action was much slower.

The presence of the isomaltosazone of Fischer[1] was indicated by the fact that the saccharin liquors become brown during concentration if the temperature is allowed to rise much over 50°, and by the fact that an osazone was obtained which was soluble in hot water.[2]

Considerable amounts of furfural and a little acetic acid were obtained in the distillate collected during concentration under diminished pressure. If a solution of the cellulose in the acid mixture is heated for four hours to 100° in a pressure flask, about 44 per cent. of the material is converted into a black insoluble mass, of which about 10 per cent resembles the so-called humic acids in being soluble in 4 per cent. ammonia. The water-soluble portion of the original material consists of a mixture of organic acids not yet determined.

Solutions of Cellulose in the Mineral Acids.

In comparing the solubility of the modified celluloses obtained above with that of normal cellulose it is found that the former resemble the latter in being soluble in phosphoric acid, sulfuric acid, and nitric acid (sp. gr. 1.52). Independent observation was made of the fact recently announced[3] that phosphoric acid will dissolve cellulose even when strongly diluted with acetic acid.

Cellulose treated with a solution of chlorosulfonic acid in chloroform

[1] *Ber.*, 23, 3687; 28, 3024.
[2] Compare Storer, *Chem. Zentr.*, 1900, II, 1069.
[3] Ger. Pat. 227,198 (1910).

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is converted to a dark liquid which is rapidly decomposed by the moisture of the air. Arsenic acid dissolves cellulose slowly in the cold, but more readily on warming. Selenic acid dissolves a little cellulose on heating, which is reprecipitated when the concentrated acid is poured into water

Discussion.

The solution of cellulose by the solvents here presented is closely connected with some phenomena which have long been known. The specific attraction which cellulose possesses for certain metallic salts was noticed by Runge[1] and by Crum,[2] who observed that cotton which had been dipped into solutions of alum, ferric acetate, and similar salts was able to fix a portion of the metal within itself as hydrated oxide or basic salt. A part of the acid present in the salt is liberated in this way and exerts the effect which dilute acids in general produce when they dry upon cellulose.

Cellulose will even fix noteworthy quantities of copper, lead, titanium and mercury when immersed in dilute solutions of the salts of these metals.[3] In certain stronger solutions the adsorption compound of cellulose and salt swells up, yielding a product resembling mercerized fiber. This indicates either that the surface condition of the cellulose is altered by the adsorption of the salt, or that the latter is removed from solution in a hydrated form. This phenomenon was studied by Müller with a solution of basic lead acetate,[4] by Cross and Bevan with zinc chloride,[5] and by Hübner and Pope with solutions of potassium iodide, potassium-mercuric iodide, and barium-mercuric iodide.[6] This swelling is the first stage in the solution of the cellulose in the solvents here presented. It is simply one manifestation of that attraction between the cellulose and the salt plus water, which may finally bring the fiber into solution.

In addition to the many examples already given of solution of cellulose in the presence of acids it may be added that potassium thiocyanate, melted down with a few drops of water, will dissolve cellulose at 200°.[7] Solution in this case is effected in a solution which has an alkaline reaction. In all other cases studied solution took place in acid media.

Cross and Bevan have attempted to explain the solution of cellulose in the zinc chloride reagent by stating that the process is analogous to that involved in the formation of double salts.[8] Nevertheless no such compound has ever been isolated. The assumed "amphoteric character

[1] "Farbenchemie," Berlin, 1834; Schwalbe, "Die Chemie der Cellulose," p. 82.
[2] *Ann.*, 55, 223 (1845).
[3] Schwalbe, *Loc. cit.*, 80, 81.
[4] "Die Pflanzenfazer," p. 16.
[5] "Cellulose," p. 8.
[6] *J. Soc. Chem. Ind.*, 23, 401 (1904).
[7] Compare the conflicting statements in the literature: *Lbz. Färberztg.*, 55, 19; Abstract, *Z. angew. Chem.*, 19, 689 (1906); Schwalbe, *Loc. cit.*, p. 155.
[8] Cross and Bevan, "Cellulose," p. 14.

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of the cellulose molecule" is still unproven, since it has its chief support in facts which may find an explanation as capillary phenomena. The idea has also been advanced that such solutions are due to the formation of alcoholates, but this theory is hardly admissible, since such compounds would be broken down by the strong acid employed. The most probable explanation for this class of cellulose solvents is, accordingly, the one first presented, which seeks to connect the process of solution in the reagents discussed with the phenomena of hydration and absorption in the presence of certain salts.

Summary.

It has been shown that cellulose in the form of filter-paper is soluble in concentrated aqueous solutions of certain salts, such as antimony trichloride, stannous chloride and zinc bromide. In solution in the aqueous hydrohalogen acids these salts and many others dissolve cellulose with extreme ease, as do also a few salts in formic acid and trichloroacetic acid.

The solution of the cellulose in these reagents is connected with facts previously known in a manner which may be summarized as follows:

Cellulose attracts metallic salts in solution to an extent depending on its mechanical structure and degree of hydration, on the nature and concentration of the salt, and on the temperature. This attractive force is opposed by that existing between the salt and its solvent, hence the final result is a distribution of the salt between the fiber and the solution. In concentrated solutions the attraction between the adsorption complex and the solvent may manifest itself in one of two ways, *viz.*: either the complex becomes hydrated, or else the reciprocal attraction of the solvent for the complex may bring the latter into solution. The latter effect obtains only where a high temperature is employed, or where some agent is present which, like certain dilute acids, can bring about union with water.

In support of the above view, it has been shown that cellulose modified by acids becomes soluble in certain reagents, such as an aqueous solution of calcium chloride, which are unable to dissolve cellulose not so modified. Chlorosulfonic, arsenic and selenic acids have been shown for the first time to possess the power of dissolving cellulose.

Celluloses dissolved in the acid solutions of the salts studied may be precipitated as amorphous compounds distinguished from the original material by their marked reducing properties and ease of hydrolysis. These substances have been described simply as modified celluloses until their relation to each other and to the so-called hydro- and hydral-celluloses can be determined.

One of the formates of cellulose has been studied with regard to the type of cellulose produced by its saponification by the agency of concentrated hydrochloric acid. Further action of this material converts the cellulose

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into water-soluble products, and finally into glucose, but no evidence is at hand to show that the production of this sugar can be made quantitative.

The writer desires to reserve for a future paper the study of the reducing power, dyeing capacity, and hydrolysis of the celluloses precipitable from the reagents presented, in order to determin their relations to each other, to various other modified celluloses, and to the parent substance. A further study of the process of hydrolysis will be made to ascertain what substances are present in the final stage where glucose is produced. It is hoped that some of the reagents discussed may prove useful in separating and studying various modified celluloses.

CHEMICAL LABORATORY,
UNIVERSITY OF WISCONSIN.

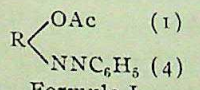
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE ACTION OF SUBSTITUTED HYDRAZINES ON β-ORTHO-TOLUQUINONE.

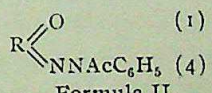
BY WILLIAM MCPHERSON AND CECIL BOORD.

Received July 3, 1911.

Notwithstanding the many investigations carried on with a view of determining the constitution of the hydroxyazo compounds and their derivatives, the question still remains an open one, except in the case of the acyl derivatives of the members of the para series.[1] These derivatives are prepared by the action of the acyl chlorides or the corresponding anhydrides on the parent hydroxyazo compounds. The problem to be solved in connection with their constitution resolves itself simply into one of determining whether the acyl group is joined to oxygen or to nitrogen as indicated in the two following formulas:



Formula I.



Formula II.

That formula I correctly represents the constitution of these derivatives was proved by the preparation of compounds having the constitution expressed in formula II. These compounds represented by formula II, in which the acyl group is joined to nitrogen, proved to be not identical but isomeric with the acyl derivatives of the corresponding parahydroxyazo compounds; hence in the latter compounds the acyl group must be joined to oxygen as shown in formula I above. The compounds of the type represented by formula II were prepared by the action of the unsymmetrical acylphenylhydrazines on the paraquinones as represented in the following equation:

[1] McPherson, *Am. Chem. J.*, 22, 364; McPherson and Gore, *Ibid.*, 25, 485.

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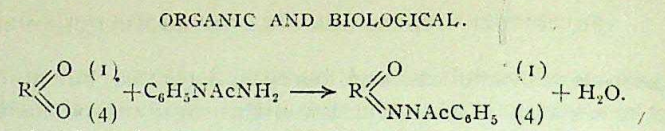
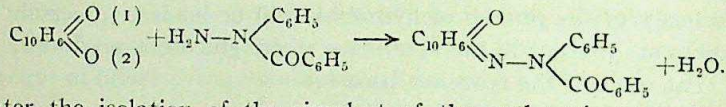
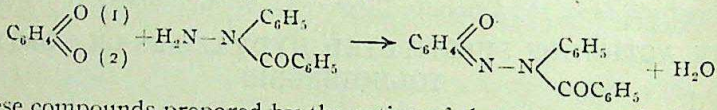


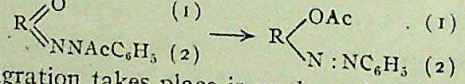
This reaction has also been extended to the orthoquinones in the hope that the question of the constitution of the orthohydroxyazo compounds might be settled in a similar way. The action of the unsymmetrical benzoylphenylhydrazine on β-naphthoquinone[1] was first studied and the results were represented by the following equations:



Later the isolation of the simplest of the orthoquinones, *viz.* orthobenzoquinone,[2] made it possible to study the reaction between this compound and the unsymmetrical benzoylphenylhydrazine.[3] This reaction is expressed by the following equation:



These compounds prepared by the action of the unsymmetrical benzoylphenylhydrazine on orthoquinones can also be prepared by the action of benzoyl chloride on the corresponding orthohydroxyazo compounds. Thus the compound obtained by the action of the unsymmetrical benzoylphenylhydrazine on orthobenzoquinone is identical with that obtained by the action of benzoyl chloride on orthohydroxyazobenzene. The conclusion is, therefore, inevitable that either the acyl derivatives of the orthohydroxyazo compounds have the acyl group joined to nitrogen or that in the reaction between the unsymmetrical acylphenylhydrazines and the orthoquinones a migration of the acyl group takes place as represented by the following equation:



That such a migration takes place is made probable from the observation of Willstätter and Veraguth[4] to the effect that the acyl derivatives of the parahydroxyazo compounds undergo a similar rearrangement when heated with a small amount of potassium hydroxide in ether solution. It would seem that if the para compounds undergo this rearrangement the ortho compounds would undergo a similar change with still greater ease. In fact it is entirely reasonable to suppose that in the case of the ortho compounds the rearrangement might take place spontaneously.

[1] McPherson, *Am. Chem. J.*, 22, 380.

[2] Jackson and Koch, *Am. Chem. J.*, 26, 10; Willstätter and Pfannesteil, *Ber.*, 1904, 4744.

[3] McPherson and Lucas, THIS JOURNAL, 31, 281.

[4] *Ber.*, 40, 1432.

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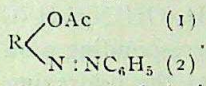
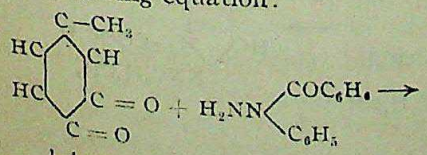
If it does not take place spontaneously, however, one would certainly expect it to take place under the same conditions which bring about the rearrangement of the para compounds. Yet these acyl derivatives of the ortho compounds undergo no change whatever under these conditions, even when heated for several hours. These facts lead to the conclusion that the acyl derivatives of the orthohydroxyazo compounds, like those of the para series, have the acyl group joined to oxygen and are therefore represented by the following formula:



On the other hand when the benzoyl derivatives of orthohydroxyazobenzene are reduced a small percentage of benzanilide is formed as one of the reduction products. This would indicate that the benzoyl group is joined to nitrogen in the original compound; otherwise it is necessary to assume a migration of the benzoyl group from oxygen to nitrogen in the process of reduction. That such a migration is probable is shown by the investigations of Auwers and Eckardt.[1]

The difficulty attending the preparation of orthobenzoquinone in sufficient quantities to study its condensation products in detail led to an attempt to isolate other orthoquinones of the benzene series in the hope that some of these might be more readily prepared and more stable than the orthobenzoquinone itself. It was also hoped that some information might be obtained in regard to the probable migration of the acyl group in the acyl derivatives of the orthohydroxyazo compounds. It is entirely reasonable to suppose that the ease with which such a migration takes place would be influenced by the presence of other substituents in the benzene ring and it was hoped in this way to find some orthoquinone which would react with the unsymmetrical acylphenylhydrazines to form a compound sufficiently stable to admit of its isolation, in which compound the acyl group remained joined to nitrogen. The isolation of such a compound would definitly prove the constitution of the acyl derivatives of the orthohydroxyazo compounds. Our experiments have shown that β-orthotoluquinone ($CH_3 : O : O = 1 : 3 : 4$) is not only more readily prepared than the orthobenzoquinone itself but that it is much more stable. A specimen of it left under a glass dish in the laboratory for two months showed only a slight darkening in color at the end of that period. This quinone reacts with the unsymmetrical benzoylphenylhydrazine in accordance with the following equation:



[1] *Ann.*, 359, 336.

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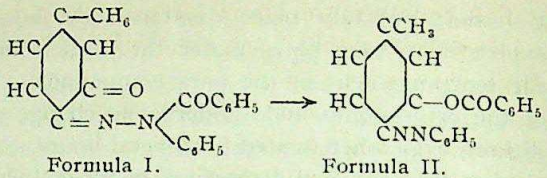
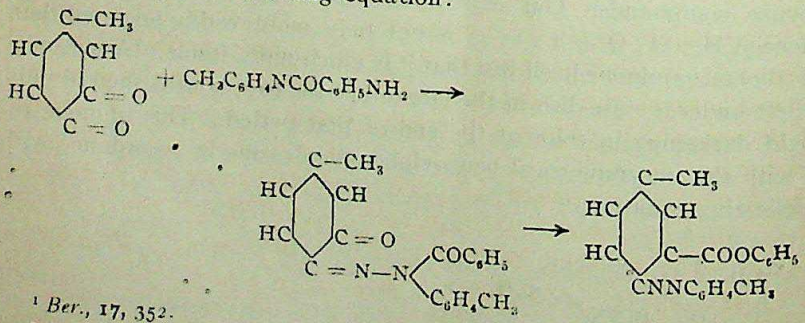


Formula I. Formula II.

That the resulting compound has the constitution expressed by formula II is shown by the following considerations. When saponified it yields benzeneazometacresol, $CH_3C_6H_3(OH)N_2C_6H_5(CH_3 : OH : N_2 = 1 : 3 : 4)$, which is isomeric with the corresponding para cresol described by Nölting and Kohn.[1] This proves that the hydrazine condenses with the oxygen which is in the para position to the methyl group in the quinone. That the acyl group is joined to oxygen rather than to nitrogen is made extremely probable from the fact that the compound undergoes no change whatever when dissolved in absolute ether to which a small amount of fused potassium hydroxide has been added and heated for several hours. Under these conditions the acyl group, if joined to nitrogen, should migrate to the oxygen atom as in the case of the corresponding para compounds. It is true on the other hand that when reduced with zinc dust and acetic acid, a very small percentage of benzanilide is formed; but the formation of this can be satisfactorily explained by the migration of the benzoyl group during reduction.[2] The particular interest in the reaction between the quinone and hydrazine was centered in the efforts to isolate the possible intermediate compound in which the benzoyl group is joined to nitrogen. All attempts to prove the formation of such a compound failed.

When benzeneazometacresol is benzoylated, there is formed benzeneazometacresol benzoate, identical in every respect with the product formed by the action of the unsymmetrical benzoylphenylhydrazine on the β-orthotoluquinone.

The action of the unsymmetrical benzoyltolylhydrazine on β-orthotoluquinone is similar to that of the corresponding phenylhydrazine and is represented by the following equation:



[1] *Ber.*, 17, 352.

[2] Auwers and Eckardt, *Ann.*, 359, 336.

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The resulting tolylazometacresol benzoate, when saponified, yields tolyl azometacresol of the following constitution: $C_6H_3(CH_3)(OH)(N_2C_6H_4CH_3)(1:3:4)$.

Experimental Part.

Preparation of β-Orthotoluquinone.—The monomethyl ester of homocatechol (kreosol) was used as the starting material in the preparation of the quinone. This ester was saponified by the action of hydriodic acid at a high temperature as described by Cousins.[1] From 50 grams of the ester there were obtained 11 grams of pure homocatechol. From this the quinone was prepared in accordance with the general method used by Willstätter and Pfannenstiel[2] in the preparation of the orthobenzoquinone. Two and one-half grams of the homocatechol were dissolved in anhydrous ether and to the solution were added 10.5 grams of silver oxide and 8 grams of fused sodium sulfate. The mixture was shaken for one hour and then filtered. The garnet-red ethereal solution upon evaporation deposited reddish-brown crystals of β-orthotoluquinone. Before the ether had entirely evaporated the crystals were filtered off and washed with ligroin.

The quinone was also prepared by treating the lead salt of homocatechol with iodine according to the method used by Jackson.[3] Ten grams of the homocatechol were dissolved in two liters of water and heated almost to boiling. To this hot solution was added a solution of 30 grams of lead acetate. The lead salt separated out and was washed a number of times by decantation. 0.5 gram of the dried salt was suspended in 25 cc. of chloroform and to this was added a solution of 3.9 grams of iodine in 125 cc. of chloroform. The mixture was shaken for about 15 minutes and the lead iodide removed by filtration. The resulting filtrate deposited the quinone on evaporation but the product was not so pure as that prepared by the method of Willstätter and Pfannenstiel. A purer product was obtained by substituting absolute ether for chloroform in the above method.

Analysis: Calculated for $C_7H_6O_2$: C, 68.83; H, 4.95.
Found: C, 68.72: H, 5.31.

β-Orthotoluquinone is a reddish-brown solid, non-volatil and practically odorless. It is easily soluble in acetone, chloroform, methyl alcohol ether and benzene and is almost insoluble in ligroin. It melts at 70–75° with decomposition. From a benzene solution it separates in clusters of needles.

The Action of Unsymmetrical Benzoylphenylhydrazine on β-Orthotoluquinone: Benzeneazometacresol benzoate, $C_6H_3(CH_3)(OC_7H_5O)(N_2C_6H_5)(1:3:4)$.—The following method gave the best results: Five grams

[1] *Compt. rend.*, 115, 234 and *Ann. chim. phys.*, 13, 532.
[2] *Ber.*, 1904, 4744.
[3] *Am. Chem. J.*, 26, 10.

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of the lead salt of homocatechol were suspended in chloroform and iodine added as described above for the preparation of the quinone. The lead iodide was removed by filtration and the resulting filtrate added directly to a solution of 3.2 grams of unsymmetrical benzoylphenylhydrazine in chloroform. The resulting mixture at once turned dark and upon spontaneous evaporation deposited an oily tar. This tar was repeatedly extracted with petroleum ether and the combined extracts upon evaporation deposited tufts of yellow needles together with a reddish oil. The mass was stirred with cold methyl alcohol, which dissolved out the oil. The remaining crystals were further purified by crystallization from ligroin. In this way 2 grams of orange-yellow needles melting sharply at 98° were obtained.

Analysis: Calculated for $C_{20}H_{16}N_2O_2$: C, 75.91; H, 5.10.
Found: C, 75.69; H, 5.23.

Benzeneazometacresol benzoate is an orange-yellow solid, very slightly soluble in cold methyl and ethyl alcohol but readily so in hot ligroin and benzene.

The Reduction of Benzeneazometacresol Benzoate.—3.94 grams of the benzoate were dissolved in about 50 cc. of glacial acetic acid. Small portions of zinc dust were added from time to time and the mixture warmed. In a few minutes the solution became almost colorless. It was decanted from the zinc and poured into water (750 cc.). On stirring there soon separated a slightly pinkish solid. This was filtered off and treated with a very dilute solution of sodium hydroxide. There remained a residue of 0.15 gram which proved to be benzanilide. Upon acidifying the alkaline solution a white flocculent precipitate (1.11 grams) was formed, which when purified melted at 159–160°. The constitution of this compound is probably expressed by the following formula: $C_6H_3(CH_3)(OH)(NHC_7H_5O)(1:3:4)$.

Saponification of Benzeneazometacresol Benzoate:—Benzeneazometacresol, $C_6H_3(CH_3)(OH)(N_2C_6H_5)(1:3:4)$.—The benzoate was saponified by dissolving in cold concentrated sulfuric acid and pouring the resulting solution into water. Benzeneazometacresol separated out and was purified by crystallizing from hot ligroin.

Analysis: Calculated for $C_{13}H_{12}N_2O$: C, 73.58; H, 5.66.
Found: C, 72.97; H, 5.80.

Benzeneazometacresol ($CH_3 : N_2 = 1 : 4$) crystallizes from hot ligroin in thin red plates melting at 122°. It is readily soluble in alcohol, benzene, acetone and chloroform. Like the other known orthohydroxyazo compounds it is very slightly soluble in alkalies. It was benzoylated by dissolving in absolute alcohol containing the theoretical amounts of sodium ethylate necessary to form the sodium salt and then adding a slight excess of benzoyl chloride. The resulting benzoate was purified

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by crystallization, first from methyl alcohol and finally from ligroin. It proved to be identical with the original benzoate prepared by the action of the unsymmetrical benzoylphenylhydrazine on β-orthotoluquinone.

The Action of Unsymmetrical:—Benzoyltolylhydrazine on β-Orthotoluquinone:—Tolylazometacresol Benzoate, $C_6H_3(CH_3)(OC_7H_5O)(N_2C_6H_4CH_3)$ (1 : 3 : 4).—This reaction with the tolylhydrazine was carried out under the same condition as with the phenylhydrazine described above. There was thus obtained an orange colored solid melting at 93°.

Analysis: Calculated for $C_{21}H_{18}N_2O_2$: C, 76.36; H, 5.45.
Found: C, 75.71; H, 5.64.

Tolylazometacresol benzoate is slightly soluble in cold methyl and ethyl alcohol and readily so in hot benzene and ligroin. It is deposited from ligroin in the form of light orange colored needles. When dissolved in sulfuric acid and the resulting solution poured into water tolylazometacresol, $C_6H_3(CH_3)(OH)(N_2C_6H_4CH_3)$(1 : 3 : 4), was deposited as an orange-red solid which on crystallization from ligroin melted at 148°.

Analysis: Calculated for $C_{14}H_{14}N_2O$: C, 74.33; H, 6.19.
Found: C, 74.24; H, 6.13.

Tolylazometacresol readily dissolves in hot ligroin, crystallizing out in the form of thin lath-shaped crystals, orange-red in color. Like the other orthohydroxyazo compounds it is very slightly soluble in alkalies. It is isomeric with the paratolylazoparacresol, $C_6H_3(CH_3)(N_2C_6H_4CH_3)(OH)$(1 : 3 : 4), described by Nölting and Kohn.[1] When benzoylated by dissolving in alcohol containing sodium ethylate and adding benzoyl chloride, tolylazometacresol benzoate is formed, identical with the compound formed by the action of the unsymmetrical benzoyltolylhydrazine on β-orthotoluquinone.

COLUMBUS, OHIO.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

HYDANTOINS: THE REDUCTION OF ALDEHYDE CONDENSATION-PRODUCTS OF 1-PHENYL-2-THIOHYDANTOIN.

[FOURTH PAPER.]

BY TREAT B. JOHNSON AND CHARLES A. BRAUTLECHT.

Received July 20, 1911.

In a previous paper from this laboratory, Wheeler and Hoffman[2] have described a new and practical method of synthesizing phenylalanine and tyrosine. They condense hydantoin with benzaldehyde and anisaldehyde, forming 4-benzal- and 4-anisalhydantoins respectively. When these unsaturated compounds are warmed with hydriodic acid they are reduced at the double bond and transformed quantitatively into the

[1] *Ber.*, 17, 354.
[2] *Am. Chem. J.*, 45, 368.

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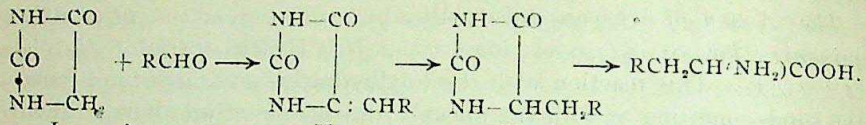
corresponding alkyl hydantoins, which are then hydrolyzed with acids or alkalies giving the α-amino-acids. This method of synthesizing an α-amino-acid is represented by the following formulas:



(R = C_6H_5 —, $CH_3OC_6H_4$ —, etc.)

Not only hydantoin I condenses smoothly with aldehydes, but it has also been observed that the methylene hydrogens of the phenylthiohydantoins V are likewise reactive towards aldehydes and these also condense with aromatic aldehydes giving the corresponding benzal-derivatives VI.[1] It was therefore of interest to determin the behavior of these aldehyde condensation products of thiohydantoins towards reducing agents. In this paper, we shall discuss only derivatives of 1-phenyl-2-thiohydantoin V.

While the aldehyde condensation products of plain hydantoin are reduced at the double bond when digested with hydriodic acid, we now find that the corresponding derivatives of 1-phenyl-2-thiohydantoin are not reduced by this reagent. Benzalphenylthiohydantoin VI, for example, was recovered unaltered after 2 hours' digestion in glacial acetic acid with an excess of iodine and red phosphorus. Also no reduction to the corresponding benzylhydantoin VII took place by the action of ferrous sulfate in an ammoniacal solution or with zinc dust and acetic acid. Aluminium amalgam effected only a partial reduction of the hydantoin. A practically quantitative transformation into the alkyl hydantoin, however, took place by reduction of the benzal hydantoins with sodium amalgam. 1-Phenyl-2-thio-4-benzal-, 1-phenyl-2-thio-4-piperonal- and 1-phenyl-2-thio-4-anisalhydantoins were converted in this manner into 1-phenyl-2-thio-4-benzyl-, 1-phenyl-2-thio-4-piperonyl- and 1-phenyl-2-thio-4-anisylhydantoins respectively.

The thiohydantoin VII, formed by reduction of 1-phenyl-2-thio-4-benzalhydantoin, VI, was identical with that obtained by the action of phenylisothiocyanate on phenylalanine,[2] IV. When this hydantoin was warmed with ethylbromide, in the presence of alkali, the corresponding 2-ethylmercapto-derivative X was formed. On hydrolysis with acids, ethylmercaptan was evolved and this compound was converted into the same substance—1-phenyl-4-benzylhydantoin, IX—as was obtained by the action of phenylisocyanate on phenylalanine.[3]

[1] Wheeler and Brautlecht, *Am. Chem. J.*, 45, 446.
[2] Brautlecht, *J. Biol. Chem.*, 10, No. 2 (1911).
[3] Mouneyrat, *Ber.*, 33, 2393.

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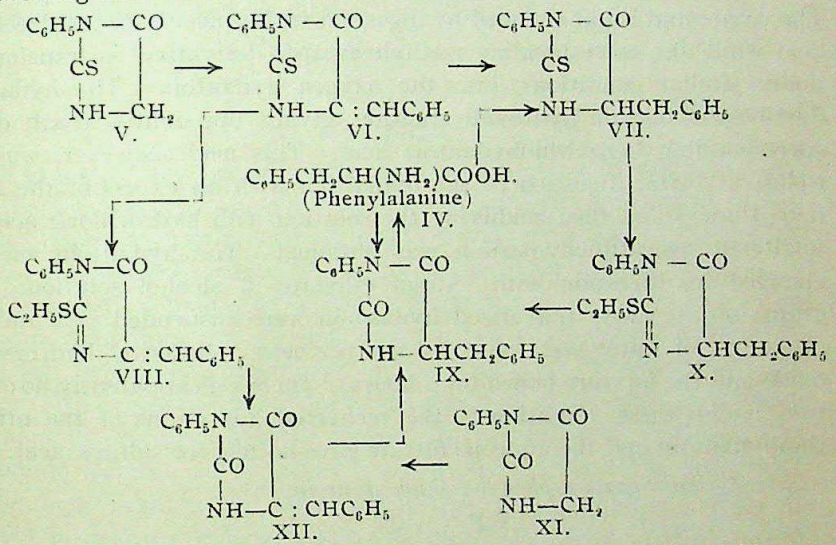
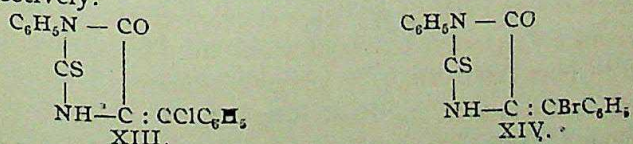
Wheeler and Brautlecht[1] have previously shown that 1-phenyl-2-thio-4-benzalhydantoin, VI, can easily be desulfurized in a similar manner, giving 1-phenyl-4-benzalhydantoin, XII. We now find that this benzal derivative, XII, is reduced smoothly by the action of sodium amalgam, giving the hydantoic acid $C_6H_5NHCONHCH(C_7H_7)COOH$.[2] This was then converted into 1-phenyl-4-benzylhydantoin, IX, by the action of hydrochloric acid. These various transformations are represented by the following structural formulas:



The 1-phenyl-2-thiohydantoin derivatives of the α-amino-acids are far more stable than the corresponding unsubstituted hydantoins studied by Wheeler and Hoffman.[2] The latter compounds underwent hydrolysis smoothly by the action of acids and alkalies, giving amino-acids. All attempts to hydrolyze, on the other hand, 1-phenyl-2-thio-4-benzylhydantoin, VII, to phenylalanine by digestion with sodium or barium hydroxide were unsuccessful. Because of this pronounced stability, the aldehyde condensation products of 1-phenylthiohydantoin are, therefore, of no value for the synthesis of amino-acids.

1-Phenyl-2-thio-4-benzalhydantoin, VI, is attacked by chlorine and bromine in glacial acetic acid solution giving 4-(α-chlorobenzal)-1-phenyl-2-thiohydantoin, XIII, and 4-(α-bromobenzal)-1-phenyl-2-thiohydantoin, XIV, respectively.



[1] *Loc. cit.*

[2] Fischer and Mouneyrat, *Ber.*, 33, 2383.

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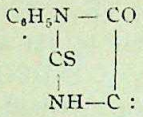
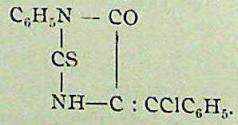
Experimental Part.

1-Phenyl-2-thio-4-benzalhydantoin,



—The method for preparing this compound has been described in a previous paper.[1] The sulfur in this hydantoin is very firmly bound. The compound is not changed by digestion with concentrated hydrochloric acid while the corresponding 2-ethylmercapto-derivative[1] is transformed, under similar conditions, into the oxygen hydantoin. The hydantoin dissolves in barium hydroxide solution, giving, apparently, a salt of the corresponding benzalthiohydantoic acid. This acid, however, was not isolated. After digestion of the hydantoin with an excess of the alkali for 10 hours and then acidifying the solution with hydrochloric acid the unaltered benzalthiohydantoin was obtained. The hydantoin was not changed by digestion with sodium ethylate in alcohol solution. Two grams of the finely pulverized hydantoin were suspended in a mixture of 400 cc. of water and 100 cc. of a 1 per cent. solution of hydrogen dioxide and the mixture boiled for 2 hours. There was apparently no oxidation under these conditions. We recovered 1.9 grams of the original thiohydantoin and the aqueous filtrate gave no test for sulfuric acid.

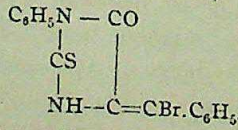
4-(α-Chlorobenzal)-1-phenyl-2-thiohydantoin,



—This compound was prepared by passing chlorine gas into cold, glacial acetic acid in which was suspended 1-phenyl-2-thio-4-benzalhydantoin. The same compound was formed whether one molecular proportion or a large excess of chlorine was used. It was purified for analysis by crystallization from acetic acid or alcohol and separated from hot solutions, on cooling, in colorless prisms, which melted at 236–237° to a clear oil. The hydantoin is very difficultly soluble in alcohol. Analysis (Kjeldahl):

Calculated for $C_{16}H_{11}ON_2SCl$: N, 8.90; found, 8.72.

4-(α-Bromobenzal)-1-phenyl-2-thiohydantoin,



—From 1-phenyl-2-thio-4-benzalhydantoin and one molecular proportion

[1] Wheeler and Brautlecht, *Loc. cit.*

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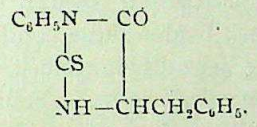
of bromine as in the preparation of the preceding chloro compound. It is soluble in boiling acetic acid, alcohol and acetone and crystallizes from alcohol in yellow plates, which melt at 211° with decomposition. The yield was about 60 per cent. of the calculated. It was dried for analysis at 100°. Analysis (Kjeldahl):

Calculated for $C_{16}H_{11}ON_2SBr$: N, 7.80; found, 7.86.

The Reduction of 1-Phenyl-2-thio-4-benzalhydantoin:

1-Phenyl-2-thio-4-benzylhydantoin,



—Forty grams of the benzalhydantoin were dissolved in dilute sodium hydroxide solution and an excess of sodium amalgam suspended in the solution. There was an immediate reaction with reduction at the double bond and the solution gradually lost its yellow color. After allowing to stand for about 19 hours, at ordinary temperature, in order to obtain a complete reduction, the solution was warmed to dissolve a crystalline sodium salt, which had separated, and the solution decanted from the mercury. An excess of hydrochloric acid was then added and the solution evaporated to dryness when the hydantoin was obtained, contaminated with sodium chloride. The salt was dissolved by trituration with water and the benzyl-hydantoin then crystallized from boiling alcohol. It separated in colorless prisms which melted at 187° to a clear oil. The yield was nearly quantitative. The hydantoin was identical with that obtained by the action of phenylmustard oil on phenylalanine.[1] A mixture of the two melted at exactly the same temperature. Analysis (Kjeldahl):

Calculated for $C_{16}H_{14}ON_2S$: N, 9.93; found, 9.89.

Attempts to reduce 1-phenyl-2-thio-4-benzalhydantoin with ferrous sulfate in ammoniacal solution, with zinc dust and acetic acid and with hydriodic acid were unsuccessful. In one experiment four grams of the benzalhydantoin were digested on the steam bath with 200 cc. of water, 300 cc. of concentrated ammonia and 2 molecular proportions of ferrous sulfate for 17 hours. We recovered, after this treatment, about 2.5 grams of pure unaltered hydantoin. Again, 4 grams of the benzalhydantoin were dissolved in 60 cc. of boiling glacial acetic acid, 2 grams of zinc dust added, and the mixture boiled for 3.5 hours. Over two grams of unaltered benzalhydantoin were recovered. In another experiment, 1.6 grams of the benzalhydantoin and 1.5 grams of iodine were dissolved in glacial acetic acid, 0.4 gram of red phosphorus suspended

[1] Brautlecht, *Loc. cit.*

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in the solution and the liquid then boiled for 2 hours. There was no evidence of a reduction and the benzalhydantoin was recovered unaltered.

Reduction with Aluminium Amalgam.—Three grams of the benzalhydantoin were dissolved in 300 cc. of dilute sodium hydroxide solution and four grams of amalgamated aluminium filings suspended in the solution. After allowing the reaction to proceed for about 18 hours and then acidifying with hydrochloric acid we obtained the benzylhydantoin mixed with unaltered material. The yield was small. The experiment was repeated and the hydantoin reduced for 60 hours with an excess of aluminium amalgam. Under these conditions, we still recovered the greater proportion of the benzalhydantoin unaltered.

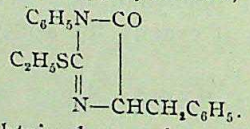
Reduction of 1-Phenyl-4-benzalhydantoin.[1]—Four grams of this hydantoin, which was prepared by the desulfurization of 1-phenyl-2-thio-4-benzalhydantoin as described in a previous paper, were dissolved in 50 cc. of dilute sodium hydroxide solution and reduced with 68 grams of 2.5 per cent. sodium amalgam. A crystalline sodium salt separated from the aqueous solution, which was first dissolved by warming, and the solution then acidified with hydrochloric acid. The corresponding hydantoic acid, $C_6H_5NH.CONHCH(CH_2C_6H_5)COOH$,[2] separated and melted at about 180°–1° with effervescence. Analysis (Kjeldahl):

Calculated for $C_{16}H_{16}O_3N_2$: N, 9.86; found, 9.88.

When this hydantoic acid was digested with hydrochloric acid it was converted into the hydantoin described by Mouneyrat,[3] melting at 173° to an oil. Analysis (Kjeldahl):

Calculated for $C_{16}H_{14}O_2N_2$: N, 10.45; found, 10.49.

1-Phenyl-2-ethylmercapto-4-benzylhydantoin,



—This hydantoin was obtained as a viscous oil by alkylation of 1-phenyl-2-thio-4-benzylhydantoin with ethylbromide in presence of sodium ethylate. It showed no signs of crystallizing after standing two days. When this mercaptohydantoin was digested with hydrochloric acid mercaptan was evolved immediately and a quantitative yield of 1-phenyl-4-benzylhydantoin[4] obtained. It melted at 180°–181° and was identical with the hydantoin obtained by reduction of 1-phenyl-4-benzalhydantoin. A mixture of the two products melted at exactly the same temperature. When 1-phenyl-4-benzylhydantoin was digested for a long time with barium hydroxide it underwent hydrolysis, giving phenyl-

[1] Wheeler and Brautlecht, *Loc. cit.*
[2] Fischer and Mouneyrat, *Loc. cit.*
[3] *Loc. cit.*
[4] Mouneyrat, *Loc. cit.*

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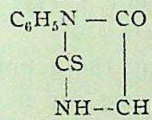
alanine, melting at 263° (N = 8.31 per cent.), carbon dioxide, aniline and, apparently, other decomposition products.

Action of Alkali on 1-Phenyl-2-thio-4-benzylhydantoin.—Attempts to hydrolyze this hydantoin to phenylalanine by digestion with sodium or barium hydroxide were unsuccessful. This stability in the presence of alkali was remarkable. Three and one-half grams of the hydantoin were suspended in a strong barium hydroxide solution and the mixture boiled on a sand-bath for 8 to 9 hours. The greater proportion of the hydantoin was recovered unaltered, while the rest had undergone decomposition giving tarry products. No phenylalanine was identified. In a second experiment, the benzylhydantoin was recovered unaltered after long digestion (8–10 hours) in strong sodium hydroxide solution.

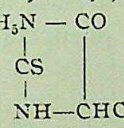
1-Phenyl-2-thiohydantoin-4-glyoxylic Acid,



—1-Phenyl-2-thiohydantoin and a molecular proportion of diethyl oxalate were dissolved in absolute alcohol containing the required amount of sodium ethylate (1 mol.). There was no apparent evidence of any reaction. After standing at ordinary temperature for 3 days the excess of alcohol was then expelled, the residue dissolved in dilute sodium hydroxide solution and the glyoxylic acid precipitated by addition of hydrochloric acid. It crystallizes from 95 per cent. alcohol as pale yellow needles, which melt at 240° with effervescence. A mixture of the acid and the original 1-phenyl-2-thiohydantoin melted at about 210°. The yield was 82 per cent. of the theoretical. Analysis (Kjeldahl):

Calculated for $C_{11}H_8O_4N_2S$: N, 10.67; found, 10.48.

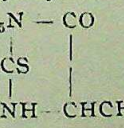
1-Phenyl-2-thio-4-(p-methoxybenzyl)-hydantoin,



—A quantitative yield of this hydantoin was obtained by dissolving 1-phenyl-2-thio-4-anisalhydantoin[1] in dilute alkali and then reducing with sodium amalgam. It crystallizes from alcohol in slender, colorless prisms, which melt at 171° to a clear oil. Analysis (Kjeldahl):

Calculated for $C_{17}H_{16}O_2N_2S$: N, 8.97; found, 8.70, 8.81.

1-Phenyl-2-thio-4-piperonyl hydantoin,



[1] Wheeler and Brautlecht, *Loc. cit.*

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—From 1-phenyl-2-thio-4-piperonalhydantoin[1] by reduction with sodium amalgam. The yield was about 70 per cent. of the calculated. It is difficultly soluble in alcohol and separates from hot solutions in straw-colored needles, which melt at 172–173° to a clear oil. It was dried for analysis at 100°. Analysis (Kjeldahl):

Calculated for $C_{17}H_{14}O_3N_2S$: N, 8.59; found, 8.57.

NEW HAVEN, CONN.

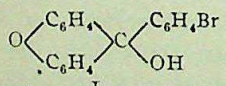
[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONDENSATION OF *p*-DIBROMOBENZENE WITH XANTHONE; A CONTRIBUTION TO THE KNOWLEDGE OF QUINOCARBONIUM SALTS.

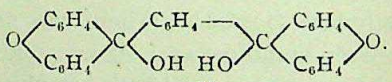
L. H. CONE AND C. J. WEST.

Received July 20, 1911.

Gomberg and Cone[2] found that by the action of xanthone upon the products resulting from dibromobenzene and magnesium two xanthenols resulted. One (I) is *p*-bromophenylxanthenol; the second (II), which they did not investigate, is *p*-phenylenedixanthenol.



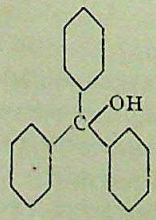
I.



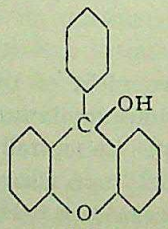
II.

This observation confirms that made by Houben,[3] who first showed that in the Barbier-Grignard reaction either one or both of the bromine atoms of *p*-dibromobenzene may react with magnesium. We have found that the reaction may be thrown largely in favor of the mono- or di-xanthenol compound, depending upon the amount of magnesium (and correspondingly of xanthone) used.

It has been shown[4] that there is a close analogy between triphenylcarbinol (III) on the one hand and phenylxanthenol (IV) on the other,



III.



IV.

[1] Wheeler and Brautlecht, *Loc. cit.*

[2] *Ann.*, **370**, 178 (1909).

[3] *Ber.*, **33**, 3796 (1905).

[4] Gomberg and Cone, *Ann.*, **370**, 142 (1909); *Ibid.*, **376**, 183 (1910); see also Gomberg and West, THIS JOURNAL, **33**, 1211 (1911).

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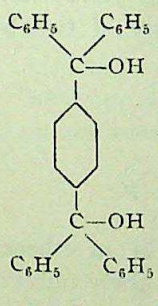
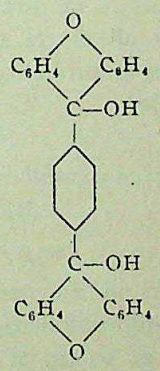
which differ only by the presence of the bridge oxygen in the latter. The general reactions of the triphenylmethane series have proven to be, with some modifications, the general reactions of the phenylxanthenol series. The increased reactivity of the xanthenols has been attributed to the bridge oxygen in the pyrone ring.

p-Phenylenedixanthenol is the simplest member of a new series of xanthenols containing, as it does, two xanthenol residues. From its constitution we would expect it to react as simple phenylxanthenol,[1] except that there would be two reactive xanthenol nuclei. Such is the case. For example, with hydrochloric acid, it yields a colored di-acid chloride, containing in all 4 atoms of chlorine; from this there may be prepared a colorless normal di-chloride, which reacts with two molecules of a metallic halide, etc.

A striking example of the influence of the bridge oxygen upon the reactions of these compounds is brought to light by a comparison of the behavior of the tetraphenylene-*p*-xylyleneglycol of Thiele[2] (V) and *p*-phenylenedixanthenol (VI), which differ in the same way as triphenyl-



V.



VI.

carbinol and phenylxanthenol. The above-mentioned glycol gives, with hydrobromic acid in acetic acid solution, a colorless bromide (VII),[3] which, with metallic silver or copper, yields a quinoid orange colored hydrocarbon, tetraphenyl-*p*-xylylene[4] (VIII), which is not at all an analog of triphenylmethyl. The reaction may be represented as follows:

[1] *Ann.*, 370, 153 (1909).

[2] Thiele and Balhorn, *Ber.*, 37, 1463 (1904). Ullmann and Schlaepfer, *Ber.*, 37, 2001 (1904).

[3] Ullmann and Schlaepfer (*loc. cit.*) have prepared the colorless chloride also by the action of dry hydrochloric acid gas upon the glycol in benzene solution.

[4] Staudinger, *Ber.*, 41, 1355 (1908), and Chichibabin, *Ber.*, 41, 2770 (1908), have also prepared this hydrocarbon.

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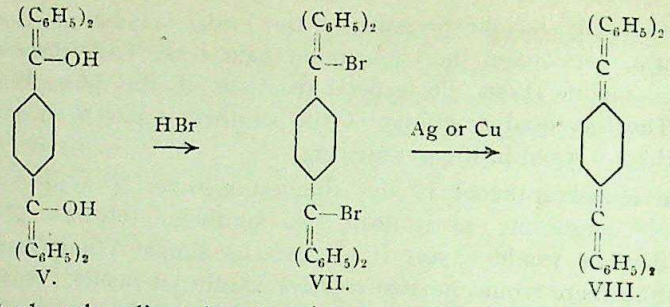
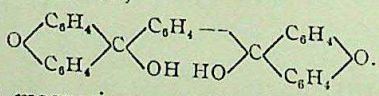


The *p*-phenylenedixanthenol, on the other hand, gives with hydrochloric acid a colored dihydrochloride, from which a colorless simple chloride may be prepared. Molecular silver removes the chlorine from this chloride, forming an unsaturated hydrocarbon, which is a true isolog of triphenylmethyl. With hydrobromic acid this xanthenol gives a colored dihydrobromide. Every attempt to prepare a colorless bromide by driving off the extra molecules of hydrobromic acid from this hydrobromide has thus far proved unavailing. A colored compound was always obtained. This is in direct contrast to simple phenyl xanthenol and, in fact, nearly all of its analogs, which readily yield colorless bromides. This deviation is probably due to the presence of two bridge oxygens in the molecule.

Experimental Part.

I. p-Phenylenedixanthenol,



—Three grams of magnesium are dissolved in an ethereal solution of 20 grams of *p*-dibromobenzene and 10 grams of finely pulverized xanthone (or dissolved in 50 cc. of boiling benzene) are gradually added to the solution. The reaction product separates out as a yellow powder soon after all the xanthone is added. After heating the mixture an hour on the water bath it is decomposed as usual. To separate the two xanthenols the following method was used:[1] The dry, crude xanthenol mixture as it comes from the Barbier-Grignard reaction is dissolved in benzene, a few cc. of acetyl chloride added, and hydrochloric acid gas passed into the solution. When the first bubble of gas strikes the solution, a bright red powder begins to separate on the walls of the flask. After the gas has been passed through the solution a few minutes, the red powder is filtered out, and the gas again passed into the solution. If more of the red powder is formed, the process is repeated until finally the solution remains a clear, pure yellow. The red powder is the hydrochloride of *p*-phenylenedixanthenol, while the solution contains the hydrochloride

[1] Gomberg and Cone, *Ann.*, 370, 179 (1909).

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of *p*-bromophenylxanthenol. The hydrochloride of *p*-phenylenedixanthenol thus obtained is hydrolyzed by boiling with ether and dilute sodium hydroxide, the ether solution dried, and evaporated to dryness. The carbinol is taken up in benzene, and the hydrochloride again precipitated, to free from any of the monoxanthenol compounds which might have been carried down at first. After hydrolyzing, the xanthenol is recrystallized from benzene and petroleum ether. Colorless crystals, melting at 176–177°, to a clear, colorless liquid. Soluble in benzene, ether, acetone, acetic ester, acetic acid, slightly soluble in alcohol, very slightly so in petroleum ether.

Calculated for $C_{32}H_{22}O_4$: C, 81.67; H, 4.71. Found: C, 81.60; H, 4.90.

Molecular weight determinations:

(1) Freezing point method, using benzene as a solvent:

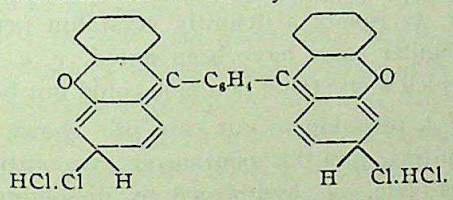
	s. Grams.	S. Grams.	*d.*	Mol. wt.
I	0.0800	12.155	0.072	457.1
II	0.1799	12.155	0.165	446.3
III	0.2802	12.155	0.255	452.0

(2) Boiling point method, using the same solvent:

	s. Grams.	S. Grams.	*r.*	Mol. wt.
I	0.2306	15.252	0.0927	446.1
II	0.7072	15.252	0.2924	434.0

Calculated molecular weight of $C_{32}H_{22}O_4$: 470.18.

p-Phenylenediquinoxanthenol-chloride hydrochloride,



The hydrochloride is best prepared by passing dry hydrochloric acid gas over a dry, fairly dilute benzene solution of the xanthenol containing a little acetyl chloride. It separates as a bright red, finely crystallin powder. The crystallin hydrochloride is filtered and dried in a stream of dry air and finally in dry hydrochloric acid gas. The excess of hydrochloric acid is then removed by dry air (two or three minutes) and the substance analyzed.

Calculated for $C_{32}H_{20}O_2Cl_2(HCl)_2$: Cl_4, 24.45. Found: Cl, 24.33.

The substance loses hydrochloric acid slowly, as a sample which had stood over night in a desiccator showed a loss of about three per cent.

If dry air is passed through a suspension of the hydrochloride in dry benzene two molecules of hydrochloric acid are gradually given off, but if the benzene is heated to boiling the evolution of hydrochloric acid is much more rapid. When exactly two molecules are removed a clear,

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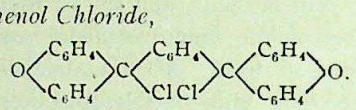
colorless solution of the chloride remains. The amount of acid driven off was estimated by passing the air through a solution of silver nitrate.

Calculated for $C_{32}H_{20}O_2Cl_2(HCl)_2$: 2HCl, 12.59. Found: HCl, 12.48.

p-Phenylenedixanthenol Chloride,



—The chloride may be prepared by concentrating the colorless benzene solution obtained as above and adding petroleum ether. It separates as colorless crystals, which, however, gradually turn pink when exposed to moist air. In the absence of moisture they may be kept indefinitly with little change. The chloride begins to darken at 210° and melts at 259–260° to a dark brown liquid.

Calculated for $C_{32}H_{20}O_2Cl_2$: Cl_2, 14.00. Found: Cl, 14.05.

Action of Molecular Silver on the Colorless Chloride.—A sample of the chloride was dissolved in benzene and sealed with molecular silver. At once the surface of the silver showed a red coloration and the solution became reddish yellow. After shaking for three days, the solution had a purplish fluorescence in reflected light, while by transmitted light a thin layer appeared a reddish yellow color. The solution was decanted from the mixture of silver and silver chloride and filtered. On exposure to the air the solution rapidly lost its color, due to the oxidation by the air of the unsaturated colored analog of triphenylmethyl. We were not able, however, to isolate a definitly crystallin peroxide from this solution. Other similar cases have been noted, *e. g.*, phenyldinaphtoxanthenol[1] from which a crystallin peroxide could not be obtained.

The presence of a peroxide in our case was shown as follows: The brown residue, resulting from the spontaneous evaporation of the benzene solution of the peroxide, was hydrolyzed by dissolving in 90 per cent. sulfuric acid and allowing to stand over night. The reaction product was decomposed with ice water and the carbinol extracted with ether. It was identified by the melting point and characteristic reactions. This has been shown to be a general reaction for the peroxides.[2]

Ferric Chloride Double Salt.—This may be prepared from a solution of the colorless chloride in acetic ester and the theoretical amount of ferric chloride dissolved in the same solvent.[3] Or, it can be prepared by dissolving the xanthenol in glacial acetic acid, saturating the solution with hydrochloric acid gas, and then adding a solution of ferric chloride in

[1] Gomberg and Cone, *Ann.*, **370**, 168 (1909).

[2] Gomberg, THIS JOURNAL, **22**, 765 (1900); *Ber.*, **33**, 3157 (1900); Gomberg and Cone, *Ber.*, **37**, 3542 (1904); see also Staudinger, *Ber.*, **44**, 1630 (1911).

[3] Naumann, *Ber.*, **43**, 314 (1910) says that "Eisen-chlorür" is soluble but that "Eisen-chlorid" is insoluble in acetic ester. The latter must be a misprint.

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acetic acid. It precipitates immediately from acetic ester as fine orange-red crystals which show no signs of decomposition at 250°.

Calculated for $C_{32}H_{20}O_2Cl_2(FeCl_3)_2$: Fe_2, 13.43; Cl_8, 34.12. Found: Fe, 13.30; Cl, 33.90.

Zinc Chloride Double Salt.—This was prepared as above, from the colorless chloride in acetic ester or from the hydrochloride in glacial acetic acid and zinc chloride in the same solvent. A little darker red in color than the corresponding iron salt.

Calculated for $C_{32}H_{20}O_2Cl_2(ZnCl_2)_2$: Zn_2, 16.77; Cl_6, 27.29. Found: Zn, 16.59; Cl, 27.15.

The *stannic chloride double salt* was prepared from solutions of the colorless chloride in benzene and stannic chloride in the same solvent. It separates at once as finely divided orange crystals, which form a rather difficult precipitate to filter and dry.

Calculated for $C_{32}H_{20}O_2Cl_2(SnCl_4)$: Cl_{10}, 38.18. Found: Cl, 38.00.

The *mercuric chloride double salt* is obtained by dissolving the carbinol in acetic ester, forming the colorless chloride with acetyl chloride and then treating with a solution of mercuric chloride in the same solvent. At the first drop of the chloride a red precipitate began to appear. The chloride was added until no further precipitate was formed. It was allowed to stand about an hour, and then filtered and dried as usual. Dull red crystals, which hydrolyzed rather slowly even in a normal sodium hydroxide solution, and which were quite stable in the presence of water.

Calculated for $C_{32}H_{20}O_2Cl_2(HgCl_2)_2$: Cl_6, 20.09. Found: Cl, 20.17.

Perbromide of the Chloride.—The perbromide may be prepared by adding a benzene solution (or a carbon disulfide solution) of bromine to a benzene solution of the colorless chloride. It separates immediately, as finely divided, yellow crystals; these were allowed to stand an hour and then were filtered out of contact with moisture and dried with dry air.

Calculated for $C_{32}H_{20}O_2Cl_2.Br_4$: Cl_2, 8.58; "perbromine" $Br_{4.3}$ 8.67. Found: Cl, 8.30; "perbromine," 38.31, 38.77.

Periodide of the Chloride.—This is prepared in the same way as the perbromide. It appears as a dark brown, nearly black powder, which is quite stable. Filtered and dried as usual.

Calculated for $C_{32}H_{20}O_2Cl_2.I_4$: Cl_2, 6.98; "periodine" I_4, 50.08. Found: Cl, 7.33; "periodine," 49.70, 49.69.

The Perchlorate.—A solution of the xanthenol in about equal parts of benzene and acetone is treated with a little more than the theoretical amount of 70 per cent. perchloric acid dissolved in acetone. The perchlorate separates almost immediately as fine reddish yellow crystals, which were filtered after standing over night. It is hydrolyzed slowly by cold water, more rapidly by boiling water. The liberated perchloric acid is titrated with sodium hydroxide. It does not melt at 290°.

Calculated for $C_{32}H_{20}O_2(ClO_4)_2$: $2ClO_4$, 31.32. Found: ClO_4, 31.45.

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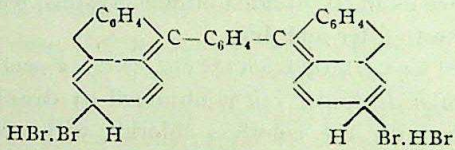
The Acid Sulfate.—One-half gram of the carbinol was dissolved in 50 cc. of absolute ether and to this a little more than the theoretical amount of sulfuric acid in the same solvent was added. At once a powder-like substance was formed, which became crystallin upon standing over night. Filtered and dried as usual. Slowly hydrolyzed with water, more rapidly with sodium hydroxide.

Calculated for $C_{32}H_{20}O_2(HSO_4)_2$: $2HSO_4$, 30.45. Found: HSO_4, 31.33.

All of the above derivatives are characterized by their great insolubility in all the ordinary solvents, and their high melting points. Not one of them begins to melt at the boiling point of sulfuric acid. They would probably decompose, if heated to a temperature between 300° and 350°.

p-Phenylenediquinoxanthenol-bromide hydrobromide,



—If acetyl bromide is added to a solution of the xanthenol in dry benzene, the first drop causes a yellow turbidity and more produces a reddish brown precipitate. Hydrobromic acid passed over the surface of this solution causes the precipitation of the dibromide as reddish brown crystals. These are filtered in a stream of dry air and finally dried in an atmosphere of dry hydrobromic acid gas.

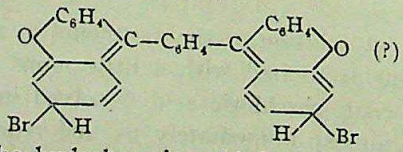
Calculated for $C_{32}H_{20}O_2Br_2(HBr)_2$: Br_4, 42.18. Found: Br, 41.22.

The hydrobromic acid is slowly given off, as after standing over night in a closed weighing bottle in a desiccator the substance had lost about 4 per cent. of hydrobromic acid.

A sample of the freshly prepared and carefully dried hydrobromide was suspended in dry xylene and a current of dry air passed through it. Hydrobromic acid was slowly given off at room temperature; the temperature was gradually raised to 80–90°, and after two hours was finally held at 110–120° for an hour. During that time two molecules of hydrobromic acid had been given off.

Calculated for $C_{32}H_{20}O_2Br_2(HBr)_2$: 2HBr, 21.35; found, 21.30.

p-Phenylenediquinoxanthenol bromide,



—After removing the hydrobromic acid from the acid bromide, as described above, there remained a red solid, insoluble in xylene. This is the simple bromide, which, unlike most halogen derivatives thus far obtained, has resisted all attempts to prepare it in the colorless form.

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The red bromide is insoluble in benzene, toluene, xylene, very slightly soluble in nitrobenzene, chloroform, and glacial acetic acid.

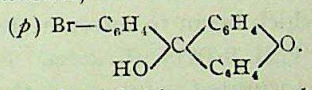
Calculated for $C_{32}H_{20}O_2Br_2$: Br_2, 26.82; found, 26.38.

If acetyl bromide is added to a solution of the xanthenol in benzene, an orange-yellow to reddish brown precipitate is formed. At the same time some hydrobromic acid is generated, due to the moisture of the solution and the air. Dry air is passed through the solution, which is heated to 80–90°, to remove the acid. The same insoluble red powder results as above. The benzene is colorless and gives no reaction with molecular silver, showing that no bromide has gone into solution. The same bromide is formed with solutions of the xanthenol in acetic ester, ether, chloroform, and to some extent in nitrobenzene and acetic acid when acetyl bromide is added.

If dry hydrobromic acid be passed into a solution of the xanthenol in glacial acetic acid the light red solution becomes a dark red, and small red crystals soon begin to appear. These are washed and dried as usual. They appear to be a mixture of the bromide and hydrobromide. This behavior is quite different from that described by Thiele for his glycol.

A small amount of a zinc bromide double salt was obtained by boiling the red bromide with chloroform, filtering hot, and adding a solution of zinc bromide in acetic ester. Red crystals. Because of the insolubility of the bromide not enough was obtained from this for analysis. A preparation in nitrobenzene gave no better results.

II. p-Bromphenylxanthenol,



—Inasmuch as a large quantity of this compound resulted as a by-product from the above work, we have prepared the following derivatives of it, in addition to those already described by Gomberg and Cone.[1] They have given the method of preparation and the properties of the xanthenol, the acid chloride, the colorless chloride, the peroxide and the perchlorate.

The Ferric Chloride Double Salt.—One-half gram of the xanthenol is suspended in 15–20 cc. of glacial acetic acid and hydrochloric acid gas passed in until solution results. An acetic acid solution of ferric chloride is added, when the double salt precipitates at once as slender yellow needles, completely filling the liquid. After standing about an hour they had become orange-yellow and more compact. The double salt is also obtained from the components in acetic ester. Readily soluble in acetone, difficultly so in acetic ester and acetic acid. Melting point, 218°.

Calculated for $C_{19}H_{12}BrOCl.FeCl_3$: Cl_4, 26.57. Found: Cl, 26.69.

The *zinc chloride double salt* may be prepared in the same way as the iron salt. It does not separate as readily from acetic acid, but does

[1] *Ann.*, 370, 178 (1909).

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so, however, after standing over night at room temperature. Large, shimmering, dark orange plates, melting at about 235° (not sharply).

Calculated for $C_{19}H_{12}BrOCl.ZnCl_2$: Cl_3, 20.95. Found: Cl, 20.97.

The stannic chloride double salt was prepared from benzene solutions of the colorless chloride and stannic chloride. A benzene solution of the hydrochloride may also be used. It appears at once upon mixing the components as dark yellow crystals. When allowed to stand, the benzene above the crystals becomes a deep red. The salt begins to soften at 155°, and melts at about 185° (not sharply).

Calculated for $C_{19}H_{12}BrOCl.SnCl_4$: Cl_5, 28.05. Found: Cl, 28.78.

The mercuric chloride double salt may be prepared from the components in acetic ester. The first drop causes the orange double salt to appear. Filtered and dried as usual. Light orange-yellow crystals which, when heated to 160°, turn a bright yellow, begin to soften at 250°, and melt to a dark red liquid at 257°.

Calculated for $C_{19}H_{12}BrOCl.HgCl_2$: Cl_3, 16.16. Found: Cl, 16.03.

The perbromide of the chloride appears slowly as fine, glistening, light orange needles from a solution of the components in carbon disulfide. Begins to melt at 190° and is completely melted at 201–202°, at which temperature bromine is evolved.

Calculated for $C_{19}H_{12}BrOCl.Br_2$: Br_2, 30.08. Found: Br, 29.80.

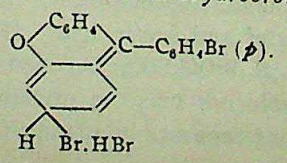
The Periodide of the Chloride.—The chloride in a mixture of benzene and carbon disulfide is treated with a solution of iodine in carbon disulfide. From the dark colored solution the iodide gradually appears in dark purple shining needles, which begin to soften at 180°, and melt at 188°.

Calculated for $C_{19}H_{12}BrOCl.I_2$: I_2, 40.59. Found: I, 40.00.

The Acid Sulfate.—A saturated solution of the xanthenol in absolute ether is treated with sulfuric acid, likewise dissolved in ether, until no further precipitation occurs. At first a yellow powder appeared, but as more acid is added this changes to a light red oil, which separated and formed a layer on the sides of the flask. This slowly became crystallin, forming rosets or large plates. The crystals are filtered and washed with careful exclusion of moisture, since they are extremely hygroscopic and are very easily decomposed by water. The large plates are brown in transmitted light and have a green metallic luster in reflected light. They melt at 77–78°.

Calculated for $C_{19}H_{12}BrO.HSO_4.H_2SO_4$: $2SO_4$, 36.18. Found: SO_4, 35.82.

p-Bromophenylquinoxanthenol-bromide Hydrobromide,



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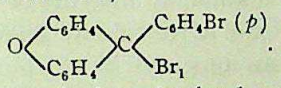
Upon adding acetyl bromide to a solution of the xanthenol in dry benzene, a slight red coloration occurs, due to a little hydrobromic acid; when dry hydrobromic acid gas is now passed over the solution, oily red drops are formed, which soon become crystallin. If a hot solution of the xanthenol is used the hydrobromide remains in solution but appears as soon as the solution is cooled under the water tap. The solution is saturated with the acid, and after adding a little petroleum ether, is allowed to stand a few hours. Filtered in the absence of moisture and finally dried in dry hydrobromic acid gas. Dark orange-red crystals, which are very hygroscopic.

Calculated for $C_{19}H_{12}BrOBr.HBr$: Br_2, 32.11. Found: Br, 31.89

A molecule of hydrobromic acid can easily be driven off by passing dry air through a suspension of the acid bromide in dry benzene, at a temperature of 60–70°. The resulting solution is clear, but has a slight yellow color.

Calculated for $C_{19}H_{12}BrOBr.HBr$: HBr, 16.29. Found: HBr, 15.99.

p-Bromophenylxanthenol bromide,



The practically colorless solution obtained as above described is concentrated and petroleum ether added. The colorless bromide is obtained in crystallin form. It is very easily affected by moisture of the air, so that it becomes coated with a red layer of the hydrobromide immediately upon exposure to the air.

Calculated for $C_{19}H_{12}BrOBr$: Br, 15.49. Found: Br, 15.60.

The zinc bromide double salt is prepared from an acetic ester solution of its components, or from an acetic acid solution of the hydrobromide and zinc bromide. Bright red crystals, melting at 250° to a dark red liquid.

Calculated for $C_{19}H_{12}BrOBr.ZnBr_2$: Br_3, 37.40. Found: Br, 37.45.

The mercuric bromide double salt may be prepared from an acetic ester solution of the components. Yellow crystals, melting at 247–248° to a dark red liquid.

Calculated for $C_{19}H_{12}BrOBr.HgBr_2$: Br_3, 34.45. Found: Br, 34.00.

The bromide perbromide is obtained as orange crystals from a solution of the components in benzene or carbon disulfide. It separates at first as an oil, which soon became crystallin. Begins to soften at 185°, and melts at 188°.

Calculated for $C_{19}H_{12}BrOBr.Br_2$: Br_3, 41.64; Br_2, 27.76. Found: Br, 41.40; Br, 27.60.

The bromide periodide precipitates as a dark red oil when the components in benzene are mixed. This very soon becomes crystallin. A deeper purple than the corresponding chlorine compound, but has the

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same shining crystallin surfaces. Melts at 211–212° to a dark purple liquid.

Calculated for $C_{10}H_{12}BrOBr.I_2$: I_2, 37.89. Found: I, 37.50.

In conclusion we wish to thank Prof. M. Gomberg, of this laboratory, for his kindly interest and many helpful suggestions during the progress of this investigation.

ANN ARBOR, MICH.

NEW BOOKS.

Essentials of Volumetric Analysis. By HENRY W. SCHIMPF. Second Edition, rewritten and enlarged. New York: John Wiley & Sons. London: Chapman & Hall. pp. 358. Price, $1.50.

The first edition of this book was primarily intended for the use of students of pharmacy. This edition will appeal to a wider circle of readers and is a marked improvement. The treatment follows in the main the lines laid down by Mohr. Analyses are classed as by Neutralization, Precipitation, Oxidation and Reduction. Then follows a second part on the estimation of alkaloids; assaying of vegetable drugs; phenol; fats; sugars; formaldehyde. After this we have a third part on a few gasometric analyses, and an appendix in which indicators are described.

EDWARD HART.

A Research on the Pines of Australia. By RICHARD T. BAKER, F.L.S., and HENRY G. SMITH, F.C.S. Published by Government of the State of New South Wales.

A magnificently printed volume of the Technical Education Series, No. 16, has appeared under the above title by Richard T. Baker, economic botanist and curator of the Technological Museum of Sydney, and Henry G. Smith, assistant curator and economic chemist. The volume is a record of pioneer work done by the authors on a number of species of the pine family indigenous to that country. No less than thirteen genera and thirty-nine species were studied, some of them for the first time.

The larger part of the volume is devoted to structural, botanical and chemical work with numerous photographs and colored plates. The chemical work follows the botanical descriptions and is, for the most part, a simple chemical examination of the oils, terpenes and resins, including the sp. gr., optical rotation, refractive index and the saponification and iodine values, when possible. Some attention has also been given to the lumbering industries.

The following general plan of work was observed under each species:

1. A field knowledge of the trees.
2. Morphology of fruit, leaves, inflorescence and their functions.
3. The anatomy of the organs.
4. Anatomy, nature and character of the timber and bark.

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5. The chemical and physical properties of the oils, gums, oleoresins, oleo-gum resins, tans and other properties that would assist in establishing natural affinities or differences in the species.

A large part of the book is given to the genus callitris. No less than eighteen different species have been described. The authors have completely reclassified the genus and studied a number of new species. It would not be within the bounds of the review to discuss the botanical work in detail. The chemical work, however, is of considerable interest not only to the industrial but also to the organic chemist. Among the many interesting facts may be mentioned: (1) The presence of a manganese compound of the resin in all of the species. The authors believe that the manganese in these species shows a strong resemblance to that in the fossil woods of past geological times.

(2) The optical rotation of the terpenes from the leaves of some of the species is in the opposite direction to that obtained from the fruit, even if collected from the same tree. So far as is known, this is the first time the fact has been noted.

(3) The acetic ester of geraniol is more pronounced in the leaf oil than is the borneol and it continues to increase until a maximum of over 60 per cent. is reached in *C. Tasmanica*.

(4) The limonenes and the dipentenes occur in the leaf oil. The leaf oil is in many cases comparable with the best "Pine Needle Oil" of commerce.

(5) The characteristic odor of the callitris is shown to be due to a phenol. It appears to be the constituent which renders the callitris timber proof to white ants.

(6) The resins vary widely; however, several of them agree closely with the sandarac resin of commerce.

From work done, the authors believe that the genus callitris will eventually be of inestimable value to Australia and will doubtless play an important part in the forestation of land which can not in the future be used successfully for farming purposes. In addition to the value as timber, several species are rich in the tannins, yielding from 14–30 per cent. Some of the species also yield sandarac resins but no methods have yet been devised for their collection.

The genus araucaria has also been studied but not so exhaustively as callitris. Only one species, a *cunninghamii* or "Hoop pine" has been exhaustively studied. This species is the largest of the Australian pines, and is of special interest on account of the high-grade timber, gums and resins it produces. The gum was found to contain two resin acids, one an isomer of abietic and the other a new acid with a formula, $C_{21}H_{33}O_3$. Unfortunately, details concerning this acid are very meager.

Phylloclandus *rhomboidalis*, another genus, is also of considerable

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interest to the chemist, inasmuch as it contains a solid di-terpene and also a sesqui-terpene. But little concerning methods of preparation and general properties is given. The di-terpene is given as crystallin with a melting point of 95°.

Agathis *robusta* is another species, the resins of which are studied. The terpenes are largely pinene. The resin acids, on the contrary, were distinct. An acid, dundathic, $C_{21}H_{53}O_5$, and dundatholic, $C_{19}H_{28}O_2$, were obtained. The author depended entirely upon the combustion of the free acid and the determination of silver in the silver salt for the formula. To one familiar with the extreme difficulties experienced in the isolation of the pure resin acids, the work seems hardly sufficient to settle on the formula of a new resin acid. A molecular weight determination should have been made, if possible, and other salts, as for example, the calcium and barium salts, prepared and analyzed before finally settling on the formulas.

The conclusions drawn by the authors are of considerable interest to the botanical chemist and emphasize the absolute necessity of cultivating the various species of the pine family if, in the future, the supply of the terpenes and resins is to continue.

There is no good reason why, with proper cultivation, the resin and the terpene industry should not be developed and the various species of the pine family made to yield much more of both resin and the terpenes than they do at present. The highly cultivated sugar beet has been made to yield an average of 13 per cent. of sugar, whereas the old uncultivated beet averaged but 3 per cent. Similar results in resins and the terpenes may be obtained by the forester, with proper care. Although the authors studied the gums, resins and terpenes pretty carefully, no effort was made to explain their functions and they remain as much of a mystery as ever.

GEO. B. FRANKFORTER.

Biochemisches Handlexikon. Herausgegeben von PROF. DR. EMIL ABDERHALDEN. Vol. II. Gummisubstanzen, Hemicellulosen, Pflanzenschleime, Pektinstoffe, Huminsubstanzen, Stärke, Dextrine, Inuline, Cellulosen, Glykogen, die einfachen Zuckerarten, stickstoffhaltige Kohlenhydrate, Cyklosen, Glucoside. Berlin: Verlag von Julius Springer. 1911. Price, bound, 46.50 Marks.

The second volume of the "Biochemisches Handlexikon" is devoted entirely to the chemistry of those substances of natural or synthetic origin which are in any wise related to the carbohydrates. In the compilation of the work the field has been divided as follows: Gums, Hemicelluloses, Plant Mucilages, Pectins, and Humus Substances, by Dr. Viktor Grafe, Vienna, 113 pages. Starches, Dextrins, Carbohydrates of the Inulin Group, Celluloses, etc., by Dr. Geza Zemplen, Selmeczbanya, 142 pages. Glycogen, by Dr. Carl Neuberg and Dr. Bruno Rewald, Berlin, 10 pages. The Sugars (mono-, di-, tri-, and tetra-saccharides; alcohol

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and acid derivatives, etc.), by Dr. Carl Neuberg and Dr. Bruno Rewald, 261 pages. Nitrogenous Carbohydrates, by Dr. Geza Zemplen, 24 pages. The Cycloses (inosites, etc.), by Dr. Viktor Grafe, 28 pages. The Glucosides, by Dr. H. Euler and Dr. J. Lundberg, Stockholm, 144 pages.

The only works which have treated the same special field as Vol. II of the Handlexikon, are the "Handbuch der Kohlenhydrate," by Tollens, published in 1898 (now somewhat out of date), and the more recent "Chemie der Zuckerarten," by Lippmann, published in 1904. For a description of analytical and technical processes the Handlexikon cannot displace the work of Tollens any more than it can supplant the work of Lippmann for its wealth of descriptive matter and fulness of presentation. On the other hand for a concise and up-to-date review of the biochemistry of the carbohydrates the Handlexikon stands alone.

The authors of Vol. II of the Handlexikon have made full use of the exhaustive compilations gathered by Lippmann in his "Chemie der Zuckerarten." It is to be regretted, however, that in their use of this mass of material greater care was not taken in correcting the numerous typographical errors which have crept into Lippmann's work. A few examples of this lamentable recopying of printers' mistakes is given in the case of the formulas of a number of hydrazones and osazones.

Compound.	True formula.	Formula of Lippmann copied by Handlexicon.
l-Xylose-*p*-bromophenylosazone....	$C_{17}H_{18}Br_2N_4O_3$	$C_{17}H_{18}Br_2N_3O_4$
l-Glucose osazone.....	$C_{18}H_{22}N_4O_4$	$C_{18}H_{22}N_2O_4$
l-Gulose phenylhydrazone.....	$C_6H_{12}O_5N_2HC_6H_5$	$C_6H_{12}O_5N_2H_2C_6H_5$
d-l-Gulose phenylhydrazone.....	$C_6H_{12}O_5N_2HC_6H_5$	$C_6H_{12}O_5N_2H_2C_6H_5$
α-Glucononose phenylosazone.....	$C_9H_{16}O_7(N_2HC_6H_5)_2$	$C_9H_{18}O_7(N_2HC_6H_5)_2$
d-Mannononose phenylosazone.....	$C_9H_{16}O_7(N_2HC_6H_5)_2$	$C_9H_{18}O_7(N_2HC_6H_5)_2$
Melibiose phenylhydrazone.....	$C_{18}H_{28}N_2O_{10}$	$C_{18}H_{28}NO_{10}$

In the case of *d-l*-arabinose diphenylhydrazone, $C_{17}H_{20}N_2O_4$, Lippmann gives $C_{17}H_{20}N_4O_4$ and the Handlexikon $C_{17}H_{10}N_4O_4$; the error in Lippmann has not only been recopied but an additional blunder has crept in. Whether similar parallelisms are to be found in case of the oximes, carbazones, mercaptals, ureides, and other numerous compounds of the sugars has not been ascertained. Mistakes of this kind might have been avoided, had the original articles, rather than Lippmann's digest, been made the basis of compilation. But apart from typographical errors, which are unavoidable in a work of such magnitude, Vol. II of the Handlexikon will be found to offer many features of distinctive merit.

It is impossible to find in any monograph a fuller account of the plant gums, hemicelluloses, pectins, etc., than that contained in the 113 pages by Dr. Grafe. The same may also be said of the 144 pages devoted by Drs. Euler and Lundberg to the chemistry of the glucosides. In fact a comprehensive work upon the glucosides was wanting prior to the appear-

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ance of this part of the Handlexikon. The methodical arrangement and systematic review of the sugars and their compounds by Drs. Neuberg and Rewald will be found of especial value to those chemists who have difficulty in finding their way in Lippmann.

One very valuable feature of this volume of the Handlexikon is the unusually complete bibliography. The references to original sources are given as footnotes and make up on the average about one-fourth the space of each page. The compilers have covered all work published down to the close of 1910, so that the chemistry of the subject is brought practically up to date.

Vol. II of the "Biochemisches Handlexikon" will be of inestimable value not only to the research or physiological chemist, who is interested in the study of plant and animal carbohydrates, but also to the technical chemist who desires to keep abreast with the latest investigations in the chemistry of cellulose, starch or sugar.

In its typography the present volume of the Handlexikon is a pattern which publishers of other chemical reference books may follow with advantage.

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ABENDROTH, W.: **Leitfaden der Physik.** 4 Aufl. Leipzig: S. Hirzel. 4.50 M.

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BAYLEY, T.: **A Pocket-book for Chemists, Metallurgists, Dyers, Distillers, Brewers, Sugar Refiners, etc.** 7th Ed. New York: Spon & Co. 559 pp., $2.00.

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BOCK, O.: **Der Ziegelofen.** 3rd Aufl. Leipzig: Carl Scholtze. 8°, 2.25 M.

BORCHERS, W.: **Metallurgy: A Brief Outline of the Modern Processes for Extracting the More Important Metals.** New York: Wiley. 8°, 271 pp., $3.00.

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Jahrbuch der Naturwissenschafter, 1910-1911. Freiburg: Herdersche Verlagshandlung. 7.50 M.

Jahrbuch der Organischen Chemie Forschungsergebnisse und Fortschritte im Jahre, 1910. Stuttgart. 8°, 512 pp., 15 M.

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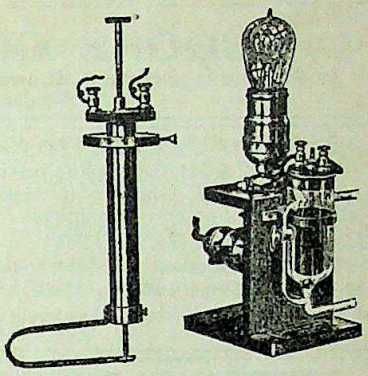

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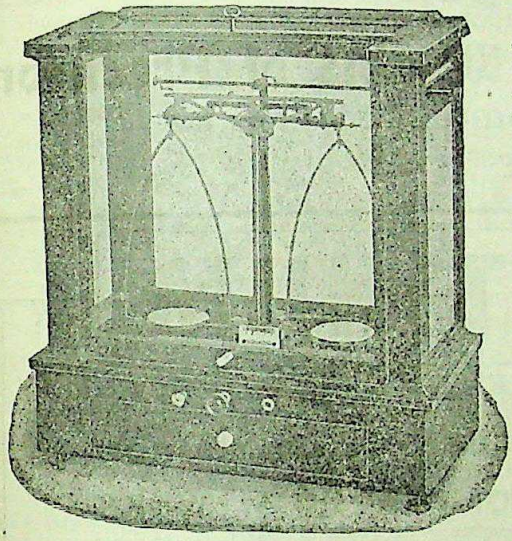

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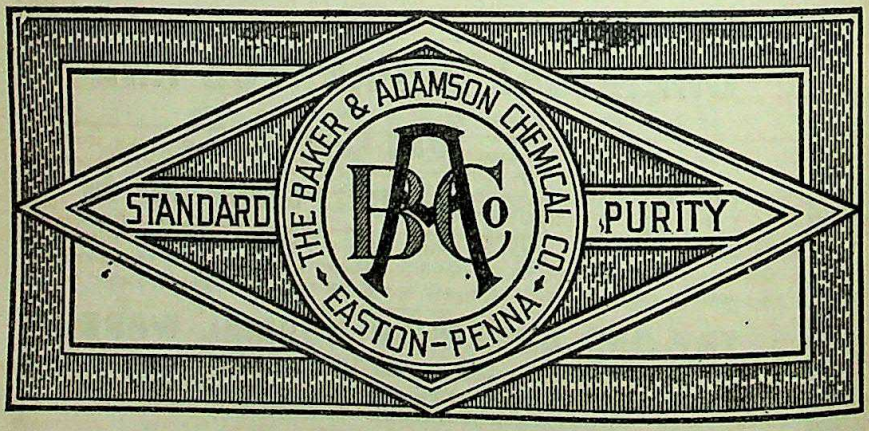

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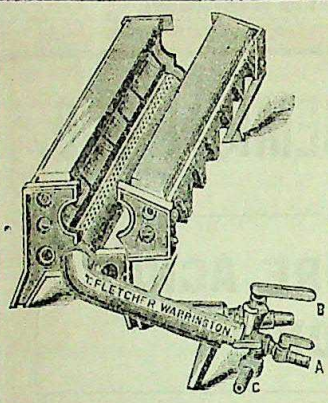

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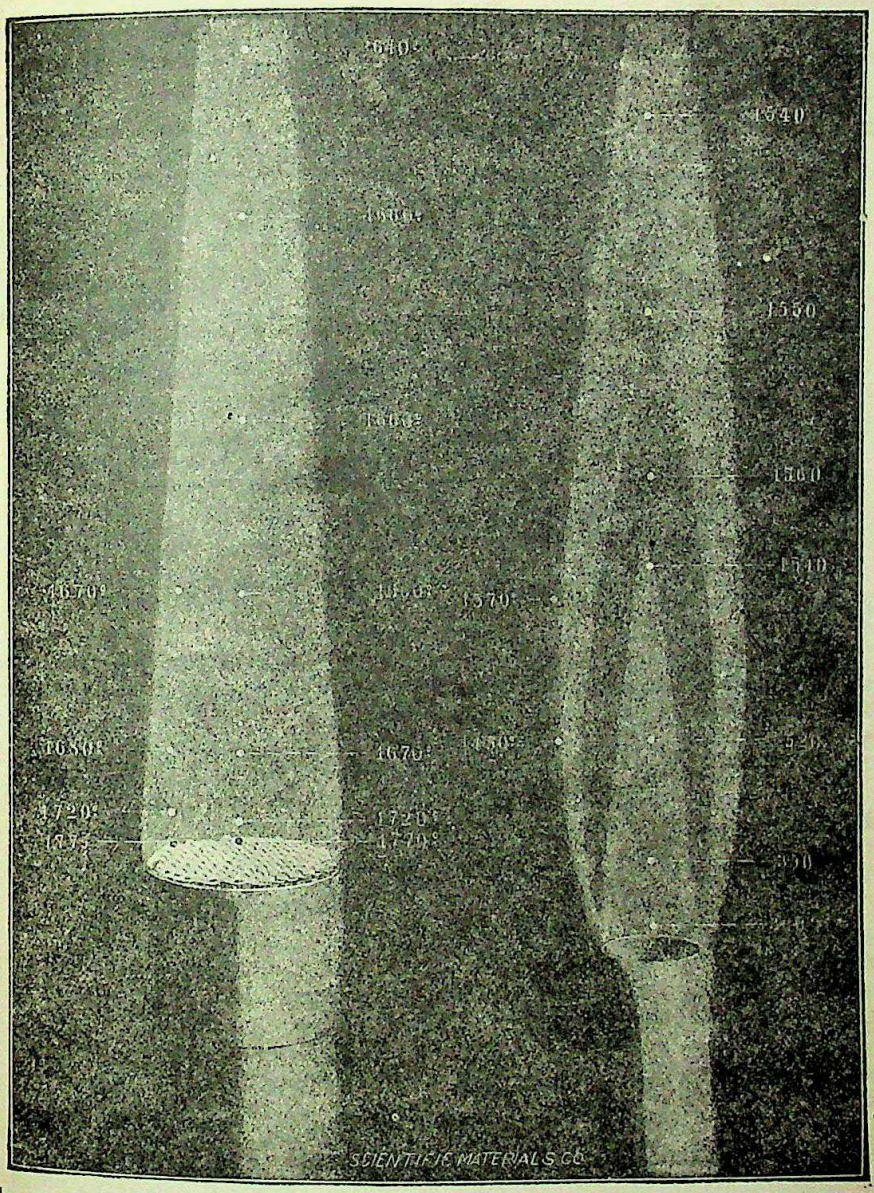

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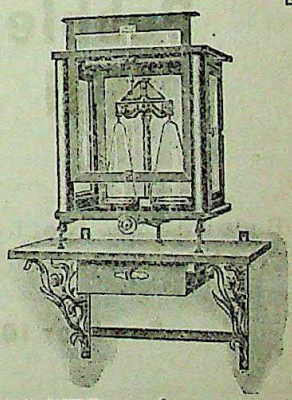

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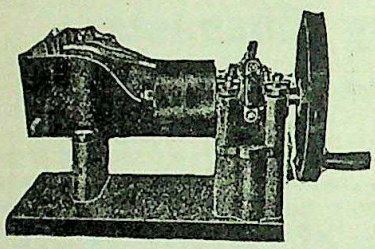

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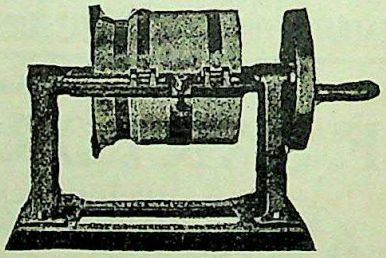

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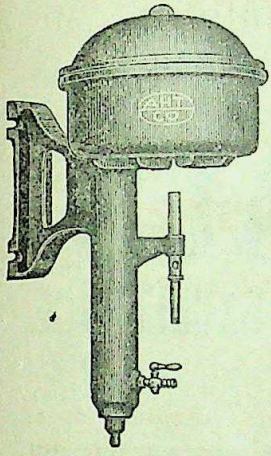

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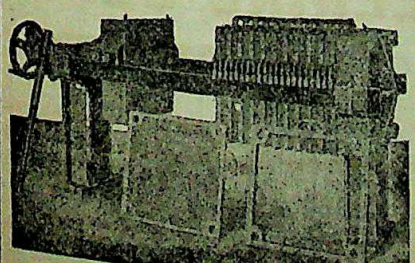

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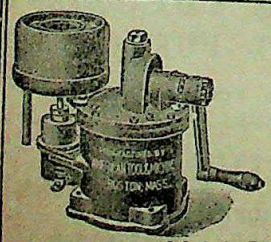

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MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

SOUTHERN CALIFORNIA SECTION.

The May meeting was held at the University Club, Los Angeles, on Thursday evening, May 18th, preceded by a dinner at 6 o'clock. The following papers were presented: "A Proposed Substitute for the Carbon Tetrachloride Test," by W. A. Brown. "Assaying," by John Herman.

The June meeting was in the form of an excursion to Riverside, where, as guests of Director J. H. Norton, the State Citrus Experiment Station was visited—thence lunch at the Glenmore Hotel, as guests of the Riverside Portland Cement Co., followed by a visit to the latter's plant. About thirty members and guests availed themselves of the day.

B. A. OLSHAUSEN, *Secretary.*

PUGET SOUND SECTION.

The June meeting was held on the 13th at the Commercial Club Rooms. Prof. Ralph S. Tarr, of Cornell University, gave a very interesting talk on "The Glaciers of Alaska."

On July 15th the Section held a basket picnic at Alki Beach, at which about thirty were present.

The Section met on August 26th, at 8 P.M., in the Faculty Club House, University of Washington. The papers for the evening were by Mr. E. Rex Smith, of the Crescent Mfg. Co., and Mr. H. M. Loomis, of the U. S. Food and Drug Laboratory, on "The Manufacture, Inspection and Analysis of Foods and Food Materials."

J. H. LINTON, *Secretary.*

CHICAGO SECTION.

The September meeting was held in the rooms of the Western Society of Engineers, on Friday evening, September 15th, at 8.00 P.M., preceded by the usual informal dinner. This first meeting of the season was a special ladies' night with an illustrated talk on "Forms of Water," with particular reference to snow and frost crystals, by Mr. William Hoskins.

D. K. FRENCH, *Secretary.*

DECEASED MEMBERS.

Professor Howard V. Frost, June 27, 1911, Chicago, Ill.
Dr. Sherman R. Macy, July 7, 1911, Des Moines, Iowa.
James Oddie, March 3, 1911, Ballarat, Victoria, Australia.
Samuel V. Peppel, August 21, 1911, Chicago, Ill.
Dr. Claude C. Perkins, August 24, 1911, New Haven, Conn.
Dr. Paul Schweitzer, University of Missouri, Columbia, Mo.

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THE OXIDATION OF HYDRAZINE. VI. REACTION BETWEEN MERCURIC OXIDE AND HYDRAZINE HYDRATE IN ALCOHOLIC SOLUTION.[1]

By C. F. HALE AND V. E. NUNEZ.

Received August 7, 1911.

Curtius and Jay[2] have noted that hydrazine hydrate explodes when dropped upon mercuric oxide. By the action of yellow mercuric oxide upon the unsymmetrical secondary hydrazines, numerous tetrazones have been prepared.[3] The behavior of hydrazine sulfate toward red and toward yellow mercuric oxide both in acid and in alkaline solution has been studied in this laboratory.[4] When heated with either red or yellow mercuric oxide, the hydrazine was found to undergo complete oxidation, without the formation of either ammonia or hydronitric acid. When yellow mercuric oxide was added a little at a time, however, to a slightly alkaline solution of hydrazine sulfate held at a temperature of 0°, appreciable amounts of both hydronitric acid and ammonia were formed.

The present work was undertaken with a view to ascertaining whether the behavior of hydrazine hydrate in alcoholic solution is analogous with the behavior of hydrazine in aqueous solution, or with the behavior of the unsymmetrical secondary hydrazines in non-aqueous solution; and also

[1] For the earlier articles of this series see Browne and Shetterly, THIS JOURNAL, 29, 1305–12 (1907); 30, 53–63 (1908); 31, 221–37 (1909); 31, 783–99 (1909); also Hale and Redfield, THIS JOURNAL, 33, 1353–62 (1911).

[2] *J. prakt. Chem.*, [2] 39, 27–58 (1889), page 43.

[3] See for example E. Fischer, *Ann.*, 190, 67–183 (1878) page 166; 199, 281–332 (1879), page 319; Renouf, *Ber.*, 13, 2169–2174 (1880); Michaelis, *Ann.*, 252, 266–317 (1889); Franchimont and Van Erp, *Rec. trav. chim.*, 14, 317–26 (1895).

[4] THIS JOURNAL, 31, 789 (1909).

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whether the nitrogen of the hydrazine is liberated quantitatively by the action of mercuric oxide, or is held back in part as ammonia, hydrazoic acid, or some other compound of nitrogen and hydrogen.

The experiments to be recorded in the present paper will be considered under two headings: (1) Gasometric study of the reaction between yellow mercuric oxide and hydrazine hydrate in ethyl alcohol, and (2) study of certain by-products of the foregoing reaction.

Gasometric Study of the Reaction between Yellow Mercuric Oxide and Hydrazine Hydrate in Ethyl Alcohol.

Materials Used.—The hydrazine hydrate, which was obtained from Raschig, was found by the method of Rimini[1] to contain 93.6 per cent. of $N_2H_4.H_2O$. The yellow mercuric oxide, obtained from the J. T. Baker Chemical Company, was found by analysis to be of a high degree of purity. It was finely pulverized before using. The ethyl alcohol, after having been boiled with quicklime for 12 hours, was found to be 99.96 per cent. pure. It was then further purified by boiling for 9 hours with solid potassium hydroxide and quicklime and by subsequent distillation. The final product gave no indication of the presence of appreciable amounts of aldehyde, when tested with the fuchsine reagent.

Apparatus Used.—The experiments of this series were carried out in a Hempel nitrometer[2] from which the weighing tube had been removed. The nitrometer was closed at the bottom by means of a one-hole rubber stopper through which connection was made with a level-bulb filled with mercury. This stopper was adequately protected by a considerable depth of mercury from the action of the hydrazine hydrate solution.

Procedure Followed.—Owing to the comparative rapidity with which the dilute alcoholic solutions of hydrazine hydrate were found to oxidize in air, it was found necessary to analyze the solutions immediately before or after each experiment. The manipulation of the nitrometer was as follows: Into the clean, dry nitrometer cylinder was introduced a weighed amount of yellow mercuric oxide 50 per cent. in excess of the quantity theoretically needed to oxidize the hydrazine in the solution used. The rubber stopper was then inserted in the bottom of the nitrometer, and was securely fastened with a clamp. Mercury was run in from the level-bulb until the side arm was covered. After 5 cc. of alcohol had been introduced through the side arm, with the precaution to prevent the lodgment of mercuric oxide in that part of the apparatus, the nitrometer was filled with mercury, and all air bubbles were carefully driven out.

Twenty-five cc. of an accurately standardized solution of hydrazine hydrate in ethyl alcohol containing from 3.28–4.57 grams $N_2H_4.H_2O$ per liter were then slowly introduced from a buret into the side arm, and the

[1] See the preceding article of this series, THIS JOURNAL, 33, 1353–62 (1911).
[2] Hempel-Dennis, "Methods of Gas Analysis," 1902, page 387.

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nitrometer was carefully shaken until the evolution of gas was complete. The evolved gas was drawn out into a water-jacketed Hempel gas buret containing mercury, above which was a small quantity of water, which served to saturate the gas with water vapor. The gas was freed from alcohol vapor by shaking in a Hempel pipet with 30 cc. of water that had been previously saturated with nitrogen, and from oxygen by shaking with alkaline pyrogallol. The volume of oxygen found varied in the experiments from 0.2–0.8 cc. The residual volume of gas was in each case measured as nitrogen, no correction being made for the volume of nitrogen that may have been dissolved in the solutions used.

The results of nine experiments are recorded in Table I.

TABLE I.

Number of experiment.	Nitrogen found (0°, 760 mm.). Cc.	Nitrogen theory. Cc.	Deficit in nitrogen. Cc.	Percentage deficit.
1.....	35.26	36.73	1.47	4.0
2.....	33.9	36.73	2.83	7.7
3.....	34.4	36.73	2.33	6.3
4.....	50.1	51.2	1.1	2.1
5.....	50.1	51.2	1.1	2.1
6.....	39.95	41.25	1.3	3.2
7.....	40.45	41.25	0.8	1.9
8.....	49.78	49.84	0.06	0.12
9.....	48.84	49.80	0.96	1.9

These results indicate that there is usually a small but appreciable deficit in the amount of gaseous nitrogen liberated at room temperature by the action of yellow mercuric oxide upon hydrazine hydrate in dilute alcoholic solution, although the reaction proceeds, under these conditions, substantially in accordance with the equation

$$N_2H_4.H_2O + 2HgO = N_2 + 2Hg + 3H_2O.$$

The residual solutions in the nitrometer were washed out with alcohol, were filtered, and were tested for hydrazine, for ammonia, and for hydronitric acid, in each case with negative results. Some other hypothesis than that of the formation of ammonia and hydronitric acid must therefore be formulated to account for the deficit in nitrogen gas.

Study of Certain By-products of the Reaction between Yellow Mercuric Oxide and Hydrazine Hydrate in Ethyl Alcohol.

The first step toward the identification of the by-products of the reaction consisted in working the reaction upon a larger scale and under conditions somewhat different from those prevailing in the nitrometer experiments.

Seventy grams of 97.6 per cent. hydrazine hydrate were dissolved in 1600 cc. of pure ethyl alcohol. The solution was constantly stirred, and

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was kept at a temperature of from —10° to —16° by means of a freezing mixture. Yellow mercuric oxide was slowly added, until, during the course of 15 hours, 425 grams had been introduced. Nitrogen gas was continuously evolved until about 400 grams of the mercuric oxide had been added. The odor of ammonia was distinctly recognized throughout the oxidation, as well as a peculiar odor resembling that of dilute witch-hazel. The mercury and the unreduced mercuric oxide were filtered off, and a 10 cc. portion of the filtrate was treated with 2 cc. of a 10 per cent. solution of concentrated sulfuric acid in ethyl alcohol, with the result that a small amount of a white crystallin precipitate was obtained. After it had been filtered off, washed with absolute alcohol, and air-dried, this precipitate was examined microchemically with the result that it was found to contain no ammonium sulfate, and that it in all probability consisted chiefly of hydrazine sulfate, or of some substance of very similar crystallin form. The alcoholic solution, before treatment with sulfuric acid, was of course incapable of reducing mercuric oxide, and was also found unable to reduce Fehling's solution, or even potassium iodate. The crystals, on the other hand, readily reduced these substances.

A larger quantity of the crystallin substance was prepared by slowly adding, to 800 cc. of the solution, 10 cc. of an alcoholic solution of sulfuric acid containing 25 grams of the acid per liter. A rather heavy white precipitate appeared first, and settled rapidly, while a finer precipitate remained in suspension. An attempt was made to separate the two precipitates by first filtering off the finer one through one paper and throwing the apparently heavier one upon another. Qualitative tests later showed, however, that the two precipitates were in all probability identical. After it had been washed with alcohol, and dried in a desiccator over solid potassium hydroxide, the substance was subjected to analysis in the special apparatus described in an earlier article.[1] The procedure consisted essentially in oxidizing the sample with a measured excess of potassium iodate, and measuring the volume of nitrogen liberated. The unused potassium iodate was then determined in the usual way. In the present instance the value of this method of effecting the simultaneous nitrometric and oxidimetric determinations lies in the fact that it affords a direct means of establishing the ratio of oxidizable hydrogen to nitrogen in the compound, and thus of distinguishing between hydrazine on the one hand, and some other oxidizable compound of nitrogen and hydrogen, or a mixture of such a compound with hydrazine, on the other.

The results of the analysis of three samples of the crystallin compound are given in Table II.

[1] THIS JOURNAL, 33, 1353–62 (1911).

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TABLE II.

Number of experiment.	Weight of sample. Gram.	Hydrogen found.		Nitrogen found.		Atomic ratio. H:N.
		Gram.	Per cent.	Gram.	Per cent.	
1.....	0.1171	0.00253	2.16	0.0180	15.37	4 : 2.04
2.....	0.1152	0.00253	2.20	0.0177	15.37	4 : 2.01
3.....	0.0933	0.00277	2.97	0.0180	19.29	4 : 2.04

In all three experiments the results in the last column indicate that the substance oxidized was hydrazine, rather than a new compound of hydrogen and nitrogen, or a mixture of such a compound with hydrazine. Tests for ammonia and hydronitric acid were made in the residual solutions, but negative results only were obtained. It will be seen, however, by inspection of the table, that the samples analyzed cannot be considered to consist entirely of hydrazine sulfate. The first two samples, which were prepared a short time before the analysis by the method outlined above, may be considered to contain, respectively, 69.8 per cent., and 70.9 per cent. of hydrazine sulfate. The third sample, which had been prepared by Dr. J. W. Turrentine during the preceding year by a similar method, and which had been stored in the meantime over solid potassium hydroxide, was found to contain 95.8 per cent. of hydrazine sulfate. The nature of the substance or substances mixed with the hydrazine sulfate has not yet been determined.

The most plausible explanation of the formation of hydrazine sulfate by treating with sulfuric acid an alcoholic solution from which all hydrazine had apparently been removed, is furnished by the recent work of Curtius and Zinkeisen.[1] These investigators found that hydrazine hydrate reacts very readily with acetaldehyde in accordance with its usual behavior toward aldehydes, with the formation of ethylidene azine. The reaction may be expressed by the equation

$$2CH_3CHO + N_2H_4 = CH_3.CH : N.N : CH.CH_3 + 2H_2O.$$

This compound, which boils at 95–96° under atmospheric pressure, was found to be fairly stable toward alkalies, but to decompose at once in acid solution, yielding acetaldehyde and the hydrazine salt of the acid used.

It cannot be stated with certainty at the present writing, whether the small amounts of acetaldehyde contained in the ethyl alcohol used as solvent are sufficient to account for the formation of the ethylidene azine, or whether, under certain conditions in the presence of hydrazine, ethyl alcohol may be oxidized by mercuric oxide to acetaldehyde. The former seems to be the more satisfactory explanation, especially in view of the fact that the alcohol used in this series of experiments was not quite so carefully purified from all but the last traces of aldehyde as was that used

[1] *J. prakt. Chem.*, [2] **58**, 310–32 (1898), page 325.

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in the gasometric work or in the work to be described below. Even in the gasometric work, however, it was found that certain of the residual solutions gave a faint white precipitate when treated with sulfuric acid. Attempts to isolate the ethylidene azine from the residual solution by fractional distillation were unsuccessful because of the small quantity of the substance present, and because of its admixture with other substances to be mentioned later.

One of the most conspicuous facts noted in connection with the oxidation experiments was the constant presence of the peculiar witch-hazel odor mentioned above. It was soon ascertained that this odor was not characteristic of ethylidene azine. Alcoholic solutions of this substance, prepared by the method of Curtius and Zinkeisen,[1] possessed an odor distinctly different from that of the substance under investigation. Moreover, the witch-hazel odor still persisted after the residual solutions had been treated with sulfuric acid. When the residual solutions, prior to treatment with sulfuric acid, were subjected to fractional distillation, the odor could readily be detected in nearly all of the fractions, but was strongest in the last fractions. No precipitate was obtained when the fractions were treated with sulfuric acid. The odor was found to persist indefinitly when the alcoholic solution of the substance was kept in a stoppered bottle. When the distillation was interrupted before the last fractions had come over, it was found that the highly concentrated residue in the distilling flask possessed an exceedingly pungent odor, and that on evaporation to dryness it yielded a waxy solid with an odor somewhat resembling that of garlic. In these preliminary experiments neither the quantity nor the purity of the substances obtained was sufficient to warrant the attempt to analyze them.

As the result of numerous blank experiments it was found that the substance possessing the witch-hazel odor was not formed: (1) when yellow mercuric oxide acted upon 93.6 per cent. hydrazine hydrate in the absence of ethyl alcohol; (2) when alcoholic solutions of acetic aldehyde, freshly prepared by distillation of paraldehyde, and of hydrazine hydrate were brought together under various conditions; (3) when ferric oxide or manganese dioxide acted upon hydrazine hydrate in alcoholic solution at room temperature; and (4) when mercuric oxide and alcohol were brought together in absence of hydrazine.

These results seemed to furnish presumptive evidence that all three compounds, mercuric oxide, hydrazine hydrate, and ethyl alcohol, contributed in some way to the formation of the compound possessing the witch-hazel odor. This led to the tentative conclusion that mercury diethyl might be the compound present.

In order to test this conclusion an alcoholic solution of mercury diethyl

[1] *Loc. cit.*

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was prepared by the method of Frankland and Duppa.[1] A rather stiff sodium amalgam was gently warmed with 20 grams of ethyl iodide and 1 gram of ethyl acetate. The reaction was carried out in a round-bottomed flask provided with a reflux condenser. Fifty cc. of absolute alcohol were added to the mass in the flask which, after prolonged shaking, was subjected to fractional distillation. The fractions collected below 78° consisted chiefly of ethyl iodide and ethyl acetate. The fractions above 78° contained varying amounts of mercury diethyl, and possessed an odor which was at once recognized as identical with that of the unknown by-product of the reaction between mercuric oxide and hydrazine hydrate in alcoholic solution. Solutions prepared directly by mixing varying amounts of pure mercury diethyl and alcohol were found to possess the same odor, while the pure substance itself showed the unmistakable, pungent, persistent odor noted in the distillation residues obtained during the fractionation of the alcoholic solutions. A sample of the pure mercury diethyl when exposed for some time to diffused daylight was found to deposit a white, waxy solid, soluble in ether and in hot alcohol, and partially decomposing when heated, to form metallic mercury, a combustible gas, and a black carbonaceous residue. A small sample of this waxy solid, when applied to the flesh, produced after several hours a painful and slow-healing burn. The substance possessed a strong, disagreeable odor, somewhat resembling that of garlic, and identical with that of the waxy solid left after evaporation to dryness of the alcoholic residues mentioned above.

In order to ascertain the conditions most favorable for the formation and isolation of the mercury compound obtained as a by-product in the oxidation of hydrazine hydrate by mercuric oxide in alcoholic solution, a series of experiments was carried out with varying concentrations of the hydrate, and at different temperatures. The resulting solution was filtered in each case, and was distilled in a special form of glass apparatus. It was found that the best yields of the waxy solid were obtained by slowly dropping an approximately 5 per cent. solution of the hydrate upon the mercuric oxide, with constant shaking, the temperature being held at the boiling point of the alcohol. Distillation of alcohol from the filtered solution was in general discontinued when the boiling point had reached 90–95°. The white solid separated out as soon as the solution had cooled or in some cases even while it was still hot. The last fractions of the distillate invariably possessed the odor of mercury diethyl, and if the temperature of the distilling flask was allowed to rize above 95° a certain amount of the white solid was carried over into the distillate.

It was not found possible, under the conditions of the experiments performed, to effect the isolation of mercury diethyl in sufficiently pure

[1] *Ann.*, 130, 105–9 (1864).

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form for analysis, but qualitative tests strongly indicated that this substance was formed in small amounts during the reaction. Attempts to isolate the white solid, however, which seems to be either a decomposition product or a reaction product of mercury diethyl, were more successful. By extraction of the solid distillation residues with ether a solution was obtained which when cautiously evaporated yielded a white, waxy solid which under the microscope presented the appearance of long curved forks and crosses. This solid, which possessed a characteristic odor somewhat similar to that of garlic, was found to be readily soluble in ether and in hot alcohol, and to be slightly soluble in water. A sample of the substance when heated in a small test tube sublimed to some extent, forming thin, iridescent plates upon the cooler portions of the tube. It also decomposed partially, yielding a small amount of a yellow, oily liquid. When rather strongly heated it decomposed more completely with a slight puff, leaving a black, carbonaceous residue and forming a cloud of white mist, which gradually settled as a deposit of minute globules of mercury. This deposit was dissolved in a few drops of aqua regia, and the presence of mercury was confirmed by means of three of the usual tests for that element.

In a second experiment a sample weighing 0.0455 gram was introduced into a glass tube which was then sealed to one of the arms of a two-way stopcock that had been fused to the capillary of a Hempel gas buret. When heated, the solid showed a tendency to sublime partially, as before, and then began to decompose, yielding first a yellow oil, and finally giving a black residue, metallic mercury, and about 3 cc. of a combustible gas. The presence of mercury, carbon, and hydrogen thus seems to be assured.

Other samples of the compound were treated with aqua regia, which was found unable to effect complete decomposition either in the cold or when heated for 6 hours in a sealed glass tube to temperatures ranging from 280–360°. A weighed sample was sealed into a thin-walled glass tube which was introduced into a combustion tube containing copper oxide, and which was broken after the copper oxide had been heated to redness. It was found that the substance when heated sublimed without apparent decomposition through about 30 cm. of red hot copper oxide.

Decomposition of the substance was finally effected by heating it with concentrated nitric acid in a sealed tube to 100–120° for 2 hours. Considerable difficulty was experienced in attempting to dry the solid for analysis. Owing to its volatility it lost weight rather rapidly on exposure to the air. Unless proper care was taken in applying heat the substance quickly assumed a dirty yellow color. It is probable, therefore, that the substance as prepared for analysis still contained small amounts of the mercury diethyl with which it had been previously asso-

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ciated, and perhaps also traces of water and of alcohol. The carefully purified samples yielded, after the treatment with nitric acid, clear yellow solutions in which the percentage of mercury was determined by the method of Volhard.[1] In one sample 53.2 per cent., and in another 56.2 per cent. of mercury were found.

The substance does not show a definit melting point. At about 160° it seems to undergo partial decomposition, yielding a yellow liquid. The residual solid turns first yellow and then brown on further heating, but gives no indication of melting at temperatures up to 260°. When applied to the flesh the substance behaved in the same way as the white solid obtained from pure mercury diethyl, producing after several hours a painful and slow-healing burn.

The smallness of the yields of the mercury compound obtained under the conditions of the experiments has made further investigation of its properties in connection with the present research seem inadvizable. During the oxidation of 20 grams of the hydrate, for example, only from 0.1–0.2 gram of the compound was obtained.

Summary.

In the present investigation it has been shown that:

(1) Hydrazine hydrate in ethyl alcohol is oxidized by yellow mercuric oxide substantially in accordance with the equation

$$N_2H_4.H_2O + 2HgO = N_2 + 3H_2O + 2Hg.$$

(2) There is usually an appreciable deficit in the percentage of nitrogen evolved, however, which is not as a rule to be explained by the formation of ammonia, or of hydronitric acid, but seems to be attributable, in part at least, to the formation of ethylidene azine.

(3) Qualitative tests indicate the formation of mercury diethyl as a by-product of the reaction, together with a white, solid compound containing carbon, hydrogen, and about 55 per cent. of mercury.

This investigation was undertaken at the suggestion of Professor A. W. Browne, and was carried out under his direction.

CORNELL UNIVERSITY, ITHACA, N. Y.

ISOMERIC INORGANIC COMPOUNDS.

BY ADOLPH LAW VOGE.

Received July 24, 1911.

Recently it has fallen to my lot to compile an index alphabetically according to condensed formulas of 15,000 inorganic compounds. In doing this many isomerisms and polymerisms were brought to light. I have thought that the new instances might be worth a note in the Journal. They are as follows:

[1] Treadwell-Hall, "Analytical Chemistry," Vol. II, first edition, p. 134.

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1. $Tl_2SO_4.Tl_2(SO_4)_3$.
   Lepsius, *Central-Blatt*, 1891, I, 694.
   $Tl_2S_2O_8$.
   Foster and Smith, THIS JOURNAL, 21, 934.
2. $Hg(NO)_2$, mercuric hyponitrite.
   Divers, *Proc. Chem. Soc.*, 1898–9, 199.
   $HgN.NO_2$, mercury nitramide.
   Thiele and Lachmann, *Ann.*, 288, 297 (1895).
3. $N(SO_3H)_2(OSO_3H)$, trisulfo-oxyazoic acid.
   Fremy, *Ann. Chem. Pharm.*, [3] 15, 408.
   Claus, *Ann.*, 158, 52 (1871).
   Raschig, *Ann.*, 241, 230 (1887).
   $NH_2OH(SO_3)_3$, hydroxylaminetrisulfonic acid.
   Haga, *J. Chem. Soc.*, 1896, 1654.
   Divers, *J. Chem. Soc.*, 1904, 108.
   $N_2H_4.H_2S_2O_6$, hydrazine bisdithionate.
   Curtius, *J. prakt. Chem.*, [2] 39, 27 (1889); 42, 521 (1890); 50, 311.
   $SO_2OH(NH_2)$, amidosulfonic acid.
   Raschig, *Ann.*, 241, 161 (1887).
   Divers and Haga, *J. Chem. Soc.*, 77, 978 (1900).
5. $Pt(NO_2)_2.2NH_3$.
   Lang, *J. prakt. Chem.*, [1] 83, 415 (1861).
   Cleve, *Nova Acta Upsala*, [3] 6, 5 (1866).
   $(Pt(NH_3)_4)Pt(NO_2)_4$.
   Magnus, Moissan, T. 5, 831.
6. $N_2H_4.H_3PO_3$, hydrazine phosphite.
   Sabanayev, *J. Russ. Phys.-Chem. Soc.*, 30, 403, 415 (1899).
   $P(NH_2)_2(OH)_3$, diamidophosphoric acid.
   Stokes, *Am. Chem. J.*, 16, 140.
   $OP(NH_2)(ONH_4)(OH)$, ammonium monoamidophosphate.
   Stokes, *Am. Chem. J.*, 15, 205.
   Sabanayev, *Z. anorg. Chem.*, 17, 486.
   $NH_2OH.H_3PO_3$, monohydroxylamine phosphite.
   Sabanayev, *J. Russ. Phys.-Chem. Soc.*, 31, 375 (1899).
   $NH_4H_2PO_4$, dihydroammonium phosphate.
   Krickmeyer, *Z. physik. Chem.*, 21, 53.
8. $HPO_2(NH_2)_2$, diamidophosphoric acid.
   Stokes, *Am. Chem. J.*, 15, 198 (1893).
   $P_2O_3(ONH_4)(NH_2)_3$.
   Gladstone and Holmes, *J. Chem. Soc.*, [2] 7, 15.
9. NH_4PO_3, ammonium metaphosphate.
   Fleitmann, *Pogg. Ann.*, 78, 233.
   $H_2PO_3(NH_2)$, amidophosphoric acid.
   Stokes, *Am. Chem. J.*, 15, 198.
   $N_2H_4.2H_2PO_3$, hydrazine bissubphosphate.
10. NH_3I, iodoammonia.
    Bineau, *Ann. chim. phys.*, 67, 228.
    $N_2H_4.2HI$, diammonium diiodide, hydrazine diiodide.
    Rothenburg, *Ber.*, 26, 865.

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11. $Cr_2(SO_4)_3.H_2SO_4$, chromosulfuric acid.
Recoura, *Compt. rend.*, 114, 477.
$(SO_3)_4Cr_2O_2(OH)_2$ or $Cr_2(SO_4)_4H_2$.
Recoura, *Compt. rend.*, 117, 37.
Wyrouboff, *Bull. soc. chim.*, [3] 27, 677.

12. $(Co(NH_3)_5(SO_3))NO_3$, sulfitocobalt pentammine nitrate.
Werner, *Z. anorg. Chem.*, 16, 410.
$(Co(NH_3)_5(NO_2))SO_4$, nitritocobalt pentammine sulfate.
Gibbs, *Proc. Am. Acad.*, 10, 5 (1875).

13. NH_4ClO, ammonium hypochlorite.
Soubeiran, *Ann. chim. phys.*, 48, 141.
Cross and Bevan, *Ber.*, 24, 689.
$NH_2OH.HCl$, hydroxylamine hydrochloride.
Lang, *Centralbl. Suppl.*, 5, 226.

14. $(Ir(NH_3)_6)IrCl_6$.
Moissan, T. 5, p. 911.
$(Cl_3Ir(NH_3)_3)$, trichloro iridium triammine.
Werner and de Vries, *Ann.*, 364, 77.

15. $Co_2(O_2)(NH)(NH_3)_6Cl_3.HCl$.
Werner, *Z. anorg. Chem.*, 21, 111.
$(Cl(NH_3)_3Co(NH_2)(O_2)Co(NH_3)_3Cl)Cl_2$.
Werner, *Ann.*, 375, 7.

16. $(Br_2Pt(NH_3)_2)$, dibromo-platinum diammine.
Peyrone, *Ann.*, 51, 1.
Odling, *Ber.*, 3, 682 (1870).
$(Pt(NH_3)_4)PtBr_4$.
Moissan, T. 5, p. 830.

17. NH_4BrO, ammonium hypobromite.
Maumené, *Compt. rend.*, 70, 147.
$NH_2OH.HBr$, hydroxylamine hydrobromide.
Adams, *Am. Chem. J.*, 28, 198.

18. $HgBr_2.2NH_3$, mercury dibromide diammine.
Naumann, *Ber.*, 42, 3789.
$NHg_2Br.3NH_4Br$.
Gaudechon, *Compt. rend.*, 148, 1763.

19. NH_2HgBr.
Loewig,
Mitscherlich, *J. prakt. Chem.*, 19, 455.
$NHg_2Br.NH_4Br$, dimercurammonium bromide.
Mitscherlich, *Ibid.*

20. $NH_4BaN(SO_3)_2$.
Divers and Haga, *J. Chem. Soc.*, 61, 966.
$Ba(SO_3NH_2)_2$, barium amidosulfate.
Berglund, *Ber.*, 9 (1896).
Lindbom, *Bull. soc. chim.*, [2] 29, 425.

21. $Cu_4As_2O_7$, cupropyroarsenate.
Reichard, *Ber.*, 31, 2166.
$2Cu_2O.As_2O_5$.
Hampe, *Z. Berg-Hütten Salinenwesen*, 22, 102 (1874).

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22. $N_2H_4.H_2C_2O_4$, acidic hydrazine oxalate.
Sabanayev, *J. Russ. Phys.-Chem. Ges.*, **31**, 378.
(Isomeric with $NH_2.CO.COOH.NH_3O$.)
$HCO_2(NH_2)$, carbamic acid (hypothetic?)
Salts of which prepared by:
Basarow, *J. prakt. Chem.*, [2] 1, 283.
Mente, *Ann.*, 248, 234 (1888).
Naumann, *Ibid.*, 150, 1 (1869).

As the properties of the compounds described were different for each pair, it seems probable that we are not dealing with the same compound under varying names and symbols.

POTASSIUM: ITS QUALITATIVE DETECTION AS THE COBALTI-NITRITE.

By Leon T. Bowser.

Received July 25, 1911.

In a previous note[1] a rapid method was outlined for the detection of potassium, even in very small amounts, by precipitating it as dipotassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6$, in the presence of ethyl alcohol. A subsequent study of its possibilities resulted in such improvement as to render it far superior to any of the commonly applied tests, and from it has been evolved a very satisfactory method for the estimation of minute amounts of potassium. The present paper will deal only with the qualitative test, however, leaving the estimation to be dealt with in a later paper.

Many qualitative tests for potassium are known but practically every one has serious shortcomings. There are almost no potassium salts even fairly insoluble in water, hence most of the tests are applicable only to very concentrated solutions. Among the reactions applied are the following: Chloroplatinic acid, H_2PtCl_6, gives with neutral or acid solutions of potassium salts, in the presence of hydrochloric acid, a yellow, crystallin precipitate of potassium chloroplatinate, K_2PtCl_6. This precipitate is soluble in about 19 parts of water at 100° C. or in 111 parts at 10°, and comparatively recent work[2] has shown its solubility in absolute ethyl alcohol at 20° to be 0.0007 gram in 100 cc. of solution. The presence of alcohol is necessary in the use of this test unless concentrated solutions be employed. The reagent also gives a precipitate with certain non-alkali bases, which must be removed previous to testing for potassium, hence this reaction is but little used for qualitative work. Sodium perchlorate, $NaClO_4$, precipitates potassium perchlorate, $KClO_4$, from solutions of potassium salts, the precipitate being slightly soluble in water but almost insoluble in strong alcohol. Potassium may also be

[1] This Journal, 32, 78 (1910).
[2] *Ibid.*, 30, 747 (1908).

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precipitated as the silicofluoride, the acid tartrate, the picrate, the phosphomolybdate and as potassium bismuth thiosulfate. Nearly every one of these reactions is far more sensitive in the presence of alcohol than of water.

Of the insoluble potassium salts there remains but one other available for qualitative purposes, namely, the cobaltinitrite. This salt, fairly complete references to the literature of which were given in an earlier paper,[1] has been known for fully half a century, but it is only within the last four years that its possibilities for the determination of potassium have been revealed to the analytical chemist. For qualitative purposes it had enjoyed some degree of usefulness, but that it possessed some unusually valuable characteristics seemed to have previously escaped attention. About the only serious attempt at a study of the reaction is that by W. C. Bray,[2] whose excellent paper served in a way as a basis for my note.[3]

The method I previously outlined was: To 5 cc. of the potassium solution add a little acetic acid, 5 cc. of sodium cobaltinitrite reagent, and then an equal amount of 95 per cent. alcohol, when the precipitate will be quickly thrown down. In this way potassium amounting to 2 parts per 100,000 could be detected within four minutes, the rapidity of the test being an important feature. It was stated that the use of alcohol did not render the precipitation any more delicate, merely hastened it so that minutes sufficed where hours were otherwise needed. The subsequent studies detailed in the present paper have proved this statement to be erroneous, and as will be shown the sensitiveness is actually increased ten times, while the time required is cut down to one or two minutes.

The merest accident led to a discovery of the fact that when two beakers are set side by side on a mirror, one containing the test being made and the other a blank test on pure water, the first will show dimness from the precipitate present that is easily apparent by comparison with the other. A development of this idea, coincident with working out the best proportions of reagents for use, gave a sensitiveness of 2 parts per million, using 5 cc. of potassium solution. Numerous trials of large beakers, test tubes, colorimeter tubes, and tall, narrow beakers showed the latter to afford the best results. Those used were of about 50 cc. capacity, and the bases were comparatively small. Beakers with smooth, flawless bottoms are preferable, as they give no distortion of the image of the observer when looking down through the solution into the mirror.

The best procedure is as follows: Pipet 5 cc. of the potassium solu-

[1] *Jour. Ind. Eng. Chem.*, 1, 791 (1909).
[2] THIS JOURNAL, 31, 621 and 633 (1909).
[3] *Loc. cit.*

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tion into a beaker of the type described, 5 cc. of distilled water into another as nearly like it as possible, and set both on a well polished mirror lying on the desk. Into each introduce 2.5 cc. sodium cobaltinitrite reagent and 5 cc. of 95 per cent. alcohol; then rotate the solutions an instant to insure thorough mixing. Looking down through the solutions into the mirror, the observer sees in the blank a bright, sharp image of himself, in the other a decidedly dim one, the dimming being caused by partial cutting off of the rays of light by the finely divided precipitate. The smaller the amount of potassium in a solution the brighter the image seen through it, until at less than 2 parts per million no decided difference can be observed between the potassium solution and the distilled water. In any case the precipitate gradually disappears and within a few minutes a potassium solution cannot be differentiated from a blank. This makes it imperative that the comparison be made quickly, else a very slight trace may never be noticed at all.

The procedure in regard to reagents differs from that given in my note to some extent, as instead of 5 cc. sodium cobaltinitrite solution only 2.5 cc. are used, while acetic acid is omitted entirely. It was found important to use as little reagent as possible, since its dark color tends to obscure the image, if in too great excess. Less than 2 cc. gives an unsatisfactory precipitation, while more than 3 cc. makes the solution too dark, but 2.5 cc. serves the purpose nicely. Experiments to determin the necessity for the addition of acetic acid showed that better results followed if it was omitted, which accords closely with the observation of Bray.[1] Any moderately strong daylight answers very well for the purposes of this test. Very sharp results may be secured if the solution be set in the direct rays of the sun, but it should be removed almost instantly, as within a short time both precipitate and reagent will be decomposed.

The following tests will serve to show the sensitiveness of the method. Volume of potassium solution taken was 5 cc. in every case.

TABLE I.

Mg. K.	Parts per million.	Precipitate perceptible.
0.15 or more	30 or more	heavy ppt. at once
0.10	20	at once
0.08	16	"
0.06	12	"
0.03	6	"
0.025	5	"
0.020	4	soon
0.015	3	"
0.010	2	within 2 minutes
0.005	1	no ppt.

[1] *Loc. cit.*

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From these results it may be seen that in most cases the presence of potassium is shown at once, while even at a dilution of 2 or 3 parts per million the precipitate will form within a minute or two. The extreme sensitiveness attained is 2 parts per million, a delicate enough test for all ordinary purposes.

It is essential that no ammonium salts be present, since they are readily precipitated by this method. Table II illustrates their behavior:

TABLE II.

Mg. NH_3.	Parts per million.	Precipitate perceptible.
0.50	100	At once
0.25	50	"
0.10	20	faintly at once
0.05	10	shortly
0.025	5	never

The extreme sensitiveness attainable in this case was found to be about 10 parts per million, or one-fifth that of potassium.

Bray states that a moderate amount of the alkaline earth elements or lithium does not interfere with the test (as conducted without alcohol), and my own results have shown that save for ammonium there is no metallic salt which interferes in any way with the precipitation so conducted. By reason of these advantages any solution may be tested directly for potassium without removing anything save ammonium. Due care must be taken in case the solution is alkaline to make it slightly acid with acetic acid. If a free acid other than acetic be present in the solution it should be neutralized by means of sodium hydroxide and then made slightly acid with acetic acid.

Summarized, the procedure is as follows: Place 5 cc. of the potassium solution in a tall beaker of 50 cc. or 100 cc. size, set on a mirror beside it 5 cc. of pure water in a similar beaker, and add to each 2.5 cc. of sodium cobaltinitrite reagent and 5 cc. of 95 per cent. alcohol. If upon looking down through the solutions into the mirror an equally sharp image of the observer can be seen in each beaker there is no potassium present; if the test solution shows a dimmer image than the blank, potassium is present amounting to two or more parts per million. The only precautions necessary are to avoid making the test in an atmosphere dense with ammoniacal fumes, to be certain of the absence of ammonium from the solution, and to be certain that the solution is neutral or slightly acid with acetic acid.

DAYTON, OHIO.

THE OXIDATION OF HYDRAZOIC ACID.

BY HAROLD EATON RIEGGER.

Received August 18, 1911.

It has been shown[1] in this laboratory that hydrazoic acid may be

[1] Browne, THIS JOURNAL, 27, 551–5 (1905); Browne and Shetterly, *Ibid.*, 29, 1305–12 (1907); 30, 53–63 (1908); 31, 221–37 (1909); 31, 783–99 (1909).

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formed in varying amounts by the oxidation of hydrazine in acid solution with a number of different oxidizing agents. In contrasting the comparatively low yields of the acid obtained by oxidation methods with the high yields secured by condensation of ethyl nitrite with hydrazine hydrate, Thiele[1] states that small yields only are obtained in the former experiments "offenbar wegen der leichten Oxydierbarkeit der Säure."

It has already been urged[2] that the variation in the amounts of ammonia formed during the oxidation of hydrazine under different conditions points to some other explanation for the lowness of the yields of hydrazoic acid than the assumption of the easy oxidizability of that compound. The most reasonable hypothesis, all things considered, seems to be the assumption of the formation of intermediate products which decompose in different ways.[3]

The present investigation was undertaken with a view to ascertaining the extent to which hydrazoic acid undergoes oxidation by certain typical substances under conditions similar to those prevailing in the experiments on the oxidation of hydrazine. In the present paper are recorded the results of a series of observations upon the behavior of hydrazoic acid in aqueous solution toward hydrogen peroxide, potassium chlorate, potassium iodate, potassium persulfate, potassium permanganate, manganese dioxide, and ferric oxide, respectively.

Materials Used.—The hydrazoic acid used in the experiments was prepared by distillation of 96 per cent. sodium trinitride (obtained from F. Raschig, Ludwigshafen) with dilute sulfuric acid, and contained 1.654 grams of hydrazoic acid per liter.

In order to facilitate comparison with the work upon the oxidation of hydrazine, the solution of hydrazoic acid used was of such strength as to contain one molecule for every two molecules of hydrazine sulfate contained in the 1 per cent. solution of that substance ordinarily employed. The solution was standardized either by the method of Dennis and Isham[4] or by a method that consists in precipitating with a slight excess of dilute silver nitrate solution, and in weighing in a Gooch crucible the resulting silver trinitride after it has been washed free from silver nitrate by means of cold water, and dried to constant weight in a vacuum desiccator over sulfuric acid.

The hydrogen peroxide solution was standardized by means of the potassium permanganate solution used in another part of the work, the latter solution having been standardized with the aid of ammonium

[1] *Ber.*, 41, 2681 (1908).

[2] THIS JOURNAL, 31, 796 (1909).

[3] For complete presentation of this hypothesis, see THIS JOURNAL, 31, 783–99 (1909), page 791 *et seq.*

[4] THIS JOURNAL, 29, 18–31 (1907), page 26.

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ferrous sulfate. The solutions of potassium chlorate, potassium iodate, and potassium persulfate were prepared by dissolving carefully weighed amounts of the ordinarily pure compounds. The remaining oxidizing agents, manganese dioxide and ferric oxide, were used in the solid form

General Procedure.—The oxidation experiments were conducted in an ordinary distillation apparatus. This consisted of a 500 cc. round-bottom flask provided with a two-hole rubber stopper carrying a 100 cc. dropping funnel and a Reitmeier bulb through which connection was established with a condenser. The receiver consisted of two 250 cc. Erlenmeyer flasks connected in series with the condenser, and so arranged that the delivery tube in each flask was immersed beneath the surface of the liquid in the flask.

In the experiments in which the oxidizing agent was used in the form of a solid, a known weight was first introduced into the distilling flask, and such a volume of the standard hydrazoic acid, that the molecular ratio of the acid to the oxidizing agent corresponded with the expression $2HN_3 : O$, was then added. In case the oxidizing agent was in the form of a solution, the hydrazoic acid was first introduced, then the oxidizing agent, the ratio of the hydrazoic acid to the oxygen being the same as before, except in the case of potassium permanganate.

In case it was decided to carry on the oxidation in the presence of sulfuric acid, that reagent was next added, having first been diluted so as to bring the total volume of the liquid in the distilling flask up to 200 cc. Otherwise, water alone was added to bring the liquid up to this volume.

The first receiving flask contained a known volume of standard sodium hydroxide, sufficient to neutralize all of the hydrazoic acid employed in the experiment. The second receiving flask contained a small measured amount of the standard alkali, and was used merely as a guard, to insure complete absorption of all hydrazoic acid.

After the reacting mixture had been permitted to stand at room temperature for about half an hour, during which period the flask was occasionally shaken, heat was gently applied until the temperature of the solution was raised to the boiling point. It was assumed that all hydrazoic acid that had escaped oxidation had been expelled from the reacting mixture after one-third[1] of the liquid had been distilled from the flask.

The contents of the receiving flasks were then mixed together and the percentage of hydrazoic acid was determined by back-titration with standard sulfuric acid, with phenolphthalein as indicator. The neutral residual solution was then in each case treated with a slight excess of dilute

[1] West, *J. Chem. Soc.*, 77, 705 (1900).

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silver nitrate solution and the resulting silver trinitride was weighed in the manner described in a preceding paragraph. The amount of unoxidized hydrazoic acid was therefore determined both volumetrically and gravimetrically.

From the foregoing it will be observed that the treatment to which the hydrazoic acid has been subjected during the present research is closely similar to that undergone by the acid in the experiments on the oxidation of hydrazine performed in this laboratory.[1]

Behavior of Hydrazoic Acid toward Hydrogen Peroxide Solution.—The hydrogen peroxide used in these experiments was the ordinary 3 per cent. Mallinckrodt product. In each experiment a volume of this solution containing 0.06535 gram of the peroxide was brought into contact with 100 cc. of the solution of hydrazoic acid. The results of the experiments are summarized in Table I.

TABLE I.

No. of expt.	Conc. H_2SO_4 used. Cc.	AgN_3 obtained. Gram.	Unoxidized HN_3 in grams. By volumetric method.	By gravimetric method.
1	0	0.5758	0.1648	0.1653
2	5	0.5759	0.1648	0.1653
3	5	0.5758	0.1648	0.1653
4	10	0.5757	0.1657	0.1653
5	10	0.5759	0.1657	0.1653
6	25	0.5754	..	0.1652
7	25	0.5755	..	0.1652
8	50	0.5758	0.1655	0.1653
9	50	0.5759	0.1653	0.1653

From these experiments it is apparent that under the prevailing conditions, hydrazoic acid does not undergo appreciable oxidation when treated with hydrogen peroxide.

Behavior of Hydrazoic Acid toward Potassium Chlorate Solution.—The solution of potassium chlorate contained 6.7424 grams of the salt per liter. In each experiment 11.65 cc. of this solution and 100 cc. of the solution of hydrazoic acid were used. In Experiments 10 and 11, the silver trinitride was weighed directly, while in Experiments 12–17, in which sulfuric acid was used, the small amounts of hydrochloric acid which distilled over with the hydrazoic acid that escaped oxidation necessitated the use of the Dennis and Isham method[2] for the determination of hydrazoic acid. The presence of hydrochloric acid in the receiver also rendered the volumetric method useless in these experiments. The results are shown in Table II.

From this series of experiments it is evident that hydrazoic acid undergoes oxidation to some extent when treated with potassium chlorate in

[1] Browne and Shetterly, *Loc. cit.*

[2] *Loc. cit.*

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neutral solution, and that in the presence of sulfuric acid the amount of oxidation increases slightly with increase in the concentration of the acid.

TABLE II.

No. of expt.	Conc. H_2SO_4 used. Cc.	AgN_3. Gram.	Unoxidized HN_3 in grams. By volumetric method.	By gravimetric method.
10	0	0.5561	0.1595	0.1597
11	0	0.5562	0.1595	0.1598
12	5	0.5469	..	0.1570
13	5	0.5449	..	0.1564
14	10	0.5435	..	0.1560
15	10	0.5438	..	0.1561
16	25	0.5422	..	0.1557
17	25	0.5414	..	0.1554

Behavior of Hydrazoic Acid toward Potassium Iodate Solution.—The solution of potassium iodate contained 12.12 grams of the salt per liter. In each experiment 11.3 cc. of the oxidizing agent and 100 cc. of the hydrazoic acid were used. In Experiments 20, 21, 22, and 23, small amounts of iodine distilled over into the receiver. This necessitated the use of the Dennis and Isham method for determination of the hydrazoic acid. In order to ascertain whether or not the liberation of iodine, which must have resulted from the decomposition of a part of the potassium iodate, was attributable to hydrazoic acid, two blank experiments were performed, in each of which 100 cc. of distilled water were substituted for the hydrazoic acid solution. In the first of these experiments, in which 10 cc. of concentrated sulfuric acid were used, a quantity corresponding to 0.0063 gram of silver iodide was liberated. In the second, in which 25 cc. of sulfuric acid were used, a yield of 0.0077 gram of silver iodide was obtained. In the first case 4.18 per cent., and in the second case 5.12 per cent. of the total amount of iodine in the potassium iodate used were set free. These results confirm the conclusion to be drawn from the data given in Table III, to the effect that hydrazoic acid does not undergo appreciable oxidation when treated with potassium iodate under the specified conditions.

TABLE III.

No. of expt.	Conc. H_2SO_4 used. Cc.	AgN_3 obtained. Gram.	Unoxidized HN_3 in grams. By volumetric method.	By gravimetric method.
18	0	0.5755	0.1653	0.1652
19	0	0.5753	0.1649	0.1652
20	10	..	0.1654	..
21	10	0.5748	0.1651	0.1650
22	25	..	0.1653	..
23	25	0.5752	0.1650	0.1652

Behavior of Hydrazoic Acid toward Potassium Persulfate Solution.—A solution containing 11.4852 grams of potassium persulfate per liter was

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used. In each experiment 45.22 cc. of this solution were brought into contact with 100 cc. of the hydrazoic acid solution. In the first two experiments, in which no sulfuric acid was used, the weight of silver trinitride was respectively 0.4790 and 0.4730 gram. The amount of unoxidized hydrazoic acid as determined by the volumetric method was found to be 0.1362 and 0.1358 gram, and by the gravimetric method 0.1375 and 0.1358 gram respectively. It is thus apparent that in the absence of sulfuric acid, hydrazoic acid is oxidized to a considerable extent by potassium persulfate. In the experiments performed in the presence of sulfuric acid it was invariably found that sulfur dioxide was liberated. This interfered greatly with the determination of the hydrazoic acid. The attempt was made to remove the sulfur dioxide quantitatively by oxidation with hydrogen peroxide solution, but the method was not found to be satisfactory. The extent to which oxidation of the hydrazoic acid took place in the experiments in which sulfuric acid was used was therefore not determined, although it is likely that oxidation was more nearly complete in the presence of sulfuric acid than in its absence.

Behavior of Hydrazoic Acid toward Potassium Permanganate Solution.—It has already been shown in this laboratory[1] that hydrazoic acid is oxidized by potassium permanganate in the presence of sulfuric acid, either in accordance with the equation

$$2KMnO_4 + 6HN_3 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 6H_2O + 9N_2 + O_2$$

or, in case the permanganate is present in excess, with the equation

$$4KMnO_4 + 2H_2SO_4 + 8HN_3 = 2K_2SO_4 + 4MnO_2 + 6H_2O + 12N_2 + O_2.$$

In the experiments performed during the present investigation, a solution of potassium permanganate containing 10.604 grams per liter was employed. Of this solution, 19.09 cc. were in each case brought into contact with 100 cc. of the hydrazoic acid solution. The results are recorded in Table IV.

TABLE IV.

No. of expt.	Conc. H_2SO_4 used. Cc.	AgN_3 obtained. Gram.	Unoxidized HN_3 in grams. By volumetric method.	By gravimetric method.
24	0	0.1665	0.0494	0.0478
25	0	0.1915	0.0513	0.0550
26	5	0.0113	0.0033	0.0032
27	5	0.0111	0.0033	0.0032
28	10	0.0099	0.0033	0.0028
29	10	0.0102	0.0033	0.0029
30	25	0.0755	0.0230	0.0217
31	25	0.0759	0.0226	0.0218
32	50	0.1261	0.0373	0.0362
33	50	0.1264	0.0393	0.0363

[1] Dennis and Browne, THIS JOURNAL, 26, 577-612 (1904), page 605.

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It is clear from these results that the maximum oxidation occurs when the sulfuric acid is comparatively dilute, and that as the concentration of the acid is increased beyond this point, the amount of oxidation is very appreciably diminished.

Behavior of Hydrazoic Acid toward Manganese Dioxide.—The manganese dioxide used was in the form of pyrolusite. The available oxygen was found by analysis to be 90.5 per cent. of theory. In each experiment 0.1845 gram of the solid oxidizing agent was brought into contact with 100 cc. of the hydrazoic acid solution. The details of the experiments are given in Table V.

TABLE V.

No. of expt.	Conc. H_2SO_4 used. Cc.	AgN_3 obtained. Gram.	Unoxidized HN_3 in grams. By volumetric method.	By gravimetric method.
34	0	0.5743	..	0.1649
35	0	0.5715	0.1636	0.1641
36	1	0.5746	0.1649	0.1649
37	1	0.5701	0.1654	0.1637
38	5	0.5664	0.1623	0.1626
39	5	0.5740	0.1644	0.1648

These experiments indicate that hydrazoic acid is oxidized to a slight but appreciable extent by the action of manganese dioxide under the specified conditions.

Behavior of Hydrazoic Acid toward Ferric Oxide.—The ferric oxide used in these experiments was found by analysis to contain 96.6 per cent. Fe_2O_3. In each case 0.6354 gram of the solid substance was treated with 100 cc. of the hydrazoic acid solution. From the results which are appended in Table VI, it is clear that no appreciable oxidation of hydrazoic acid takes place under the conditions of these experiments.

TABLE VI.

No. of expt.	Conc. H_2SO_4. Cc	AgN_3 obtained. Gram.	Unoxidized HN_3 in grams. By volumetric method.	By gravimetric method.
40	0	0.5759	0.1654	0.1653
41	0	0.5757	0.1651	0.1653
42	10	0.5750	0.1653	0.1651
43	10	0.5756	0.1652	0.1653
44	50	0.5758	..	0.1653
45	50	0.5722	..	0.1643

Discussion of Results.—On the basis of their behavior toward hydrazine sulfate in the presence of dilute sulfuric acid, certain of the more common oxidizing agents have been tentatively classified into three groups:[1] oxidizing agents of the first class comprize those which oxidize hydrazine with formation of considerable amounts of both hydrazoic acid and

[1] THIS JOURNAL, 31, 783–799 (1909), page 793.

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ammonia; those of the second class yield little or no hydrazoic acid but large amounts of ammonia; those of the third class yield little or no hydrazoic acid or ammonia.

If Thiele's idea[1] that the lowness of the yields of hydrazoic acid obtainable from hydrazine by the action of certain oxidizing agents is attributable to the easy oxidizability of hydrazoic acid be correct, it would seem reasonable to suppose (1) that oxidizing agents of the second and third classes should readily oxidize hydrazoic acid, and (2) that oxidizing agents of the first class should oxidize hydrazoic acid either not at all or only with some difficulty.

Of the oxidizing agents employed in the present investigation, those belonging to the first class are hydrogen peroxide, potassium chlorate, and potassium persulfate. While hydrogen peroxide has been shown to have no perceptible oxidizing action upon hydrazoic acid, both potassium chlorate and potassium persulfate have been found to oxidize the acid appreciably. Of the oxidizing agents belonging to the second class, potassium permanganate was found to oxidize the acid vigorously, manganese dioxide but slightly, and ferric oxide not to any appreciable extent. Potassium iodate, which belongs to the third class, does not oxidize hydrazoic acid at all under the conditions prevailing in the experiments. From these facts it is apparent that of the seven oxidizing agents studied, only two, hydrogen peroxide and potassium permanganate, behaved consistently with the explanation offered by Thiele.

Summary.

In the present investigation the action of seven oxidizing agents upon hydrazoic acid in aqueous solution has been studied under conditions duplicating as far as possible those prevailing in the oxidation of hydrazine. It has been shown (1) that potassium permanganate oxidizes hydrazoic acid vigorously, (2) that potassium persulfate oxidizes the acid to a considerable extent, (3) that potassium chlorate and manganese dioxide exert a slight but appreciable oxidizing action, and (4) that ferric oxide, hydrogen peroxide, and potassium iodate do not perceptibly oxidize hydrazoic acid.

From these results the conclusion is drawn that the comparative lowness of the yields of hydrazoic acid obtained by the action of oxidizing agents upon hydrazine is probably not to be explained on the ground that hydrazoic acid is oxidized during these reactions, as suggested by Thiele.

The present investigation was undertaken at the suggestion of Professor A. W. Browne, and carried on under his personal supervision.

CORNELL UNIVERSITY, ITHACA, N. Y.

[1] *Loc. cit.*

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TIME CURVES FOR CADMIUM DEPOSITED FROM ORGANIC ELECTROLYTES.

By Mary V. Dover.

Received June 16, 1911.

The present work is supplemental to a paper published by Holmes and Dover[1] in which it was shown that with currents below one ampere, using the rotating spiral anode, cadmium could be deposited in a more or less satisfactory form from various organic electrolytes. Because the character of the deposits varied considerably with the electrolyte used, it seemed worth while to make a series of determinations in order to show clearly the progressive deposition of the metal, and the quantity of it that could be deposited from each electrolyte in a sufficiently adhesive form to weigh accurately.

As in the previous work, a platinum dish of about 200 cc. capacity served as cathode with a spiral anode, making about 400 revolutions a minute. Solutions of cadmium salts containing about 0.2 gram of the cadmium metal in 10 cc. of solution were used in each case.

Cadmium Acetate in Acetate Electrolyte.—The most satisfactory conditions for the deposition of cadmium seemed to be as follows: Ten cc. of cadmium acetate solution were diluted to 110 cc., 0.5 cc. acetic acid (conc.) and 2 grams of ammonium acetate were added. The whole was heated to incipient boiling and electrolyzed.

Observing the above conditions, the accompanying time curve was determined.

The first nine deposits were finely crystallin, smooth and white. In No. 9 (25 min., 0.1250 gram cadmium) there was the first suggestion of a few small crystal plates adhering to the white deposit, immediately under the electrode.

Cadmium Acetate in Acetate Electrolyte.

No.	Volts.	Ampere.	Time. Min.	Wt. of Cd in grams.
1	2.4	0.3	1	0.0099
2	2.4	0.3	2	0.0144
3	2.4	0.3	3	0.0192
4	2.4	0.3	5	0.0313
5	2.4	0.3	7	0.0447
6	2.4	0.3	10	0.0576
7	2.4	0.3	15	0.0798
8	2.4–2.5	0.3	20	0.1095
9	2.4–2.6	0.3	25	0.1250
10	2.4–2.6	0.3	30	0.1399
11	2.4–2.8	0.3	35	0.1601
12	2.4–2.8	0.3	40	0.1700
13	2.4–2.8	0.3	45	0.1764

[1] This Journal, 32, 1251.

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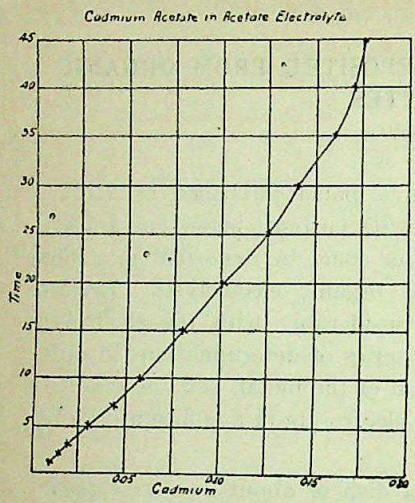

Fig. 1.

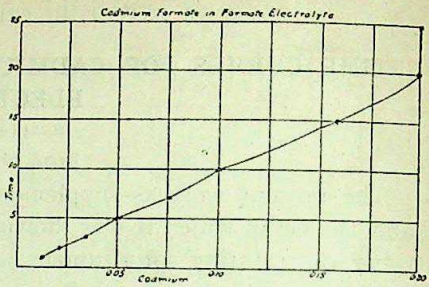

Fig. 2.

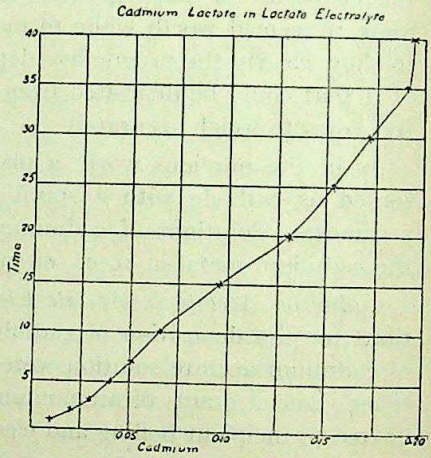

Fig. 3.

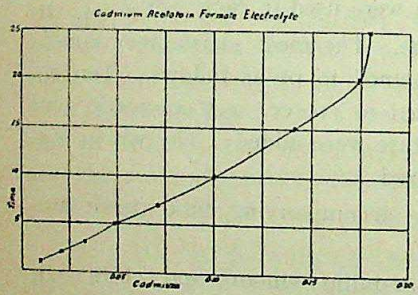

Fig. 4.

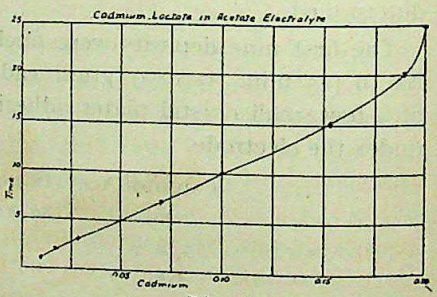

Fig. 6.

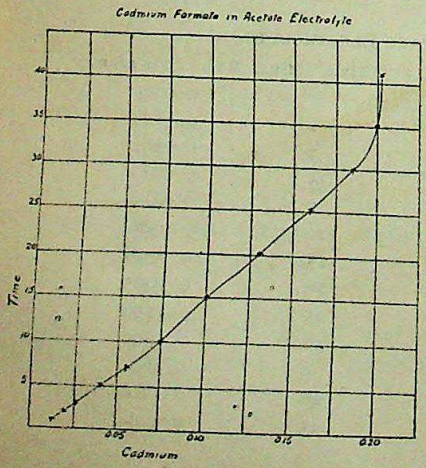

Fig. 5.

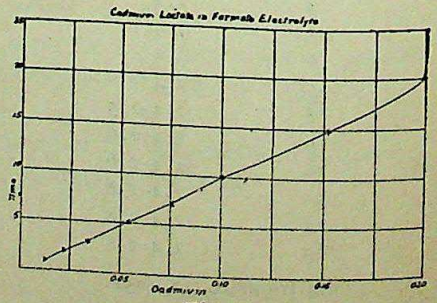

Fig. 7.

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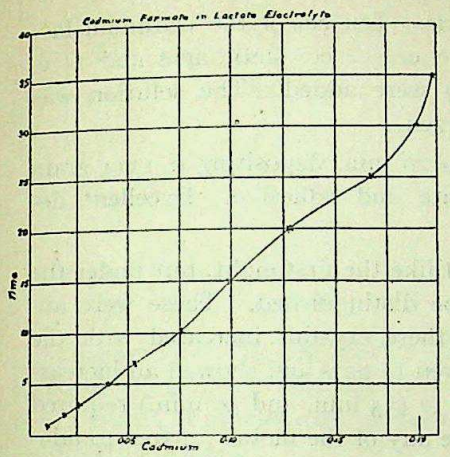

Fig. 8.

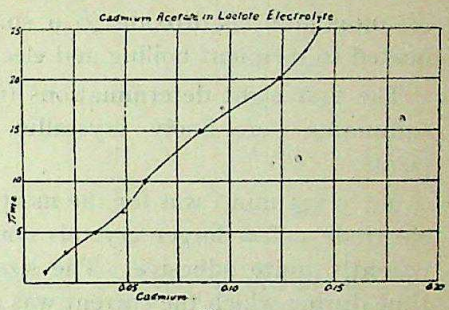

Fig. 9.

In No. 10 (30 min.) there were large crystals (plates) under the electrode, which were inclined to scale off. This was increasingly the case in Nos. 11, 12 and 13. It was necessary to wash these last three deposits with great care to avoid loss.

After 45 minutes no trace of cadmium could be detected in the solution by the addition of hydrogen sulfide.

Cadmium Formate in Formate Electrolyte.—Ten cc. of cadmium formate solution were diluted to about 110 cc.—0.5 cc. formic acid was added and 2 grams of sodium formate. The solution was kept hot during the deposition. The current was inclined to be unsteady.

In the first seven determinations (up to 15 min., 0.1577 gram Cd) the deposit was finely crystallin, white and adhesive with a few larger (adhesive) crystals immediately under the electrode.

No. 8 (20 min., 0.1938 gram cadmium), deposit as above, but crystals rather inclined to scale off.

No. 9 (25 min.), deposit as above, larger crystals inclined to scale off, though on the whole good and much more adhesive than No. 8. No trace of cadmium was found with hydrogen sulfide after twenty-five minutes.

CADMIUM FORMATE IN FORMATE ELECTROLYTE.

No.	Volts.	Ampere.	Time. Min.	Wt. Cd in grams.
1	1.4	0.3	1	0.0137
2	1.4	0.3	2	0.0218
3	1.4	0.3	3	0.0348
4	1.4	0.3	5	0.0507
5	1.4	0.3	7	0.0763
6	1.4–2.4	0.3	10	0.1025
7	1.2–2.4	0.3	15	0.1577
8	1.4–2.6	0.3	20	0.1938
9	1.4–2.6	0.3	25	0.1959

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Cadmium Lactate in Lactate Electrolyte.—Ten cc. of the cadmium lactate solution were diluted to about 110 cc.—2 cc. lactic acid and 1 cc. of ammonium hydroxide (0.9 sp. gr.) were added. The solution was heated to incipient boiling and electrolyzed.

The first eight determinations (up to 20 min. depositing 0.1314 gram cadimum) were finely crystallin, white and adhesive. Excellent deposits.

No. 9 (25 min.) was for the most part like the first eight, but under the electrode a few larger crystals could be distinguished. These were apparently quite adhesive. The size of these crystals increased with the time during which the current was allowed to pass and showed an increasing tendency to scale off. Nos. 11 and 12 (35 min. and 40 min.) required very careful washing in order not to lose any of the metal. After 40 min. the solution showed no trace of yellow coloration with hydrogen sulfide. Current unsteady.

CADMIUM LACTATE IN LACTATE ELECTROLYTE.

No.	Volts.	Ampere.	Time. Min.	Wt. Cd in grams.
1	2.6	0.3	1	0.0097
2	2.6	0.3	2	0.0185
3	2.6–2.8	0.3	3	0.0290
4	2.6	0.3	5	0.0406
5	2.6	0.3	7	0.0488
6	2.4–2.6	0.3	10	0.0658
7	2.6–2.8	0.3	15	0.0954
8	2.4–2.8	0.3	20	0.1314
9	2.5–2.8	0.3	25	0.1536
10	2.6–2.8	0.3	30	0.1713
11	2.6–2.8	0.3	35	0.1909
12	2.6–3.0	0.3	40	0.1931

Cadmium Acetate in Formate Electrolyte.—Ten cc. of cadmium acetate solution were diluted to about 110 cc.—0.5 cc. formic acid and 2 grams of sodium formate were added. The solution was heated and electrolyzed.

The first six deposits (up to ten minutes and containing 0.1050 gram of cadmium) were finely crystallin, white and adhesive. No. 7 (15 minutes containing 0.1420 gram cadmium) showed a few larger adhesive crystals immediately under the electrode.

Nos. 8 and 9 (20 minutes and 25 minutes, 0.1748 and 0.1772 gram cadmium) showed a more or less porous, adhesive deposit, grayish in color and difficult to dry.

There was no trace of cadmium upon the addition of hydrogen sulfide after the current had been passing for 25 min. The current was more or less unsteady.

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CADMIUM ACETATE IN FORMATE ELECTROLYTE.

No.	Volts.	Ampere.	Time. Min.	Wt. Cd in grams.
1	2.0	0.3	1	0.0094
2	2.0	0.3	2	0.0218
3	1.4	0.3	3	0.0330
4	2.0	0.3	5	0.0484
5	1.2	0.3	7	0.0713
6	1.0–1.6	0.3	10	0.1050
7	1.6	0.3	15	0.1426
8	1.4	0.3	20	0.1748
9	1.4–2.8	0.3	25	0.1772

Cadmium Formate in Acetate Electrolyte.—Ten cc. of the cadmium formate solution were diluted to 110 cc.—0.5 cc. acetic acid was added, also 2 grams of ammonium acetate. The solution was heated and electrolyzed as before.

Up to No. 10 (30 min., 0.1852 gram cadmium) the deposits were excellent, white, smooth, finely crystallin and perfectly adhesive.

Nos. 11 and 12 contained a few larger crystals, which were inclined to scale off, but with careful washing accurate results were obtained. After 40 min. there was no trace of cadmium upon the addition of hydrogen sulfide. Current unsteady.

CADMIUM FORMATE IN ACETATE ELECTROLYTE.

No.	Volts.	Ampere.	Time. Min.	Wt. Cd in grams.
1	2.6	0.3	1	0.0122
2	2.6	0.3	2	0.0187
3	3.2	0.3	3	0.0268
4	3.4	0.3	5	0.0401
5	2.8–3.0	0.3	7	0.0555
6	3.2–4.0	0.3	10	0.0759
7	3.0–3.2	0.3	15	0.1047
8	3.0–3.8	0.3	20	0.1301
9	2.8–3.4	0.3	25	0.1615
10	2.4–3.0	0.3	30	0.1852
11	3.4–3.8	0.3	35	0.2002
12	3.0–3.6	0.3	40	0.2024

Cadmium Lactate in Acetate Electrolyte.—Ten cc. cadmium lactate solution were diluted to about 110 cc.–0.5 cc. of acetic acid was added and 2 grams of ammonium acetate. The solution was heated and electrolyzed as before.

The first six deposits (up to 10 min., 0.1011 gram cadmium) were easily washed (adhesive, but spotted in colors). No. 7 (15 min. containing 0.1532 gram cadmium) was difficult to wash, owing to tendency to scale off. Nos. 8 and 9 (20 and 25 min., 0.1925 gram cadmium) were porous and required very careful washing to prevent loss. No trace of cadmium was found by hydrogen sulfide after 25 min. Current generally unsteady.

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CADMIUM LACTATE IN ACETATE ELECTROLYTE.

No.	Volts.	Ampere.	Time. Min.	Wt. Cd in grams.
1	2.8	0.3	1	0.0098
2	2.6	0.3	2	0.0168
3	2.6	0.3	3	0.0283
4	2.6	0.3	5	0.0449
5	2.8	0.3	7	0.0705
6	2.6	0.3	10	0.1011
7	2.6	0.3	15	0.1532
8	2.6	0.3	20	0.1897
9	2.4	0.3	25	0.1925

Cadmium Lactate in Formate Electrolyte.—Ten cc. cadmium lactate solution were diluted to about 110 cc.—0.5 cc. formic acid was added and 2 grams sodium formate. The solution was heated and electrolyzed as before.

The first seven deposits (up to 15 min., 0.1521 gram cadmium) were smooth, white and finely crystallin. Nos. 8 and 9 were as above for the most part, but showed larger gray, adhesive (apparently) crystals requiring careful drying.

CADMIUM LACTATE IN FORMATE ELECTROLYTE.

No.	Volts.	Ampere.	Time. Min.	Wt. Cd in grams.
1	1.8–2.8	0.3	1	0.0128
2	1.4–1.8	0.3	2	0.0218
3	2.4–3.8	0.3	3	0.0341
4	1.2–2.4	0.3	5	0.0543
5	1.2–2.6	0.3	7	0.0754
6	1.2–2.4	0.3	10	0.1015
7	1.0–2.4	0.3	15	0.1521
8	1.4–2.6	0.3	20	0.1969
9	1.2–2.6	0.3	25	0.2063

Cadmium Formate in Lactate Electrolyte.—Ten cc. cadmium formate solution were diluted to about 110 cc.—2 cc. lactic acid and 1 cc. ammonium hydroxide were added. The solution was heated and electrolyzed.

CADMIUM FORMATE IN LACTATE ELECTROLYTE.

No.	Volts.	Ampere.	Time. Min.	Wt. Cd in grams.
1	2.6	0.3	1	0.0089
2	2.2	0.3	2	0.0186
3	2.6	0.3	3	0.0267
4	2.6–3.0	0.3	5	0.0410
5	2.4–2.8	0.3	7	0.0531
6	2.6–2.8	0.3	10	0.0765
7	2.6–2.8	0.3	15	0.0991
8	2.4–3.0	0.3	20	0.1275
9	2.6–3.0	0.3	25	0.1673
10	2.6–3.0	0.3	30	0.1881
11	2.8–3.0	0.3	35	0.1984
12	2.4–3.0	0.3	40	0.2016

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The first eight deposits (up to 20 min., 0.1275 gram cadmium) were light colored, smooth and adhesive. Nos. 9, 10, 11 and 12 became more and more porous (due to large crystal plates) and not entirely adhesive, requiring very careful washing. Current unsteady. No trace of cadmium was found with hydrogen sulfide after 40 minutes.

Cadmium Acetate in Lactate Electrolyte.—Ten cc. cadmium acetate solution were diluted to about 110–2 cc. lactic acid and 1 cc. of ammonium hydroxide was added. The solution was heated and electrolyzed as before. An ammoniacal electrolyte was tried as above, using 1 cc. lactic acid, but the deposit was too porous to weigh, and not at all adhesive. The current was passed for one hour.

The first seven deposits (up to 15 min., 0.0866 gram cadmium) were smooth and adhesive though not so light in color as the others. These, after 15 min., showed large crystals, which scaled off. This curve varies very much and is not of much value. Current very unsteady.

CADMIUM ACETATE IN LACTATE ELECTROLYTE.

No.	Volts.	Ampere.	Time. Min.	Wt. Cd in grams.
1	3.0	0.3	1	0.0101
2	3.0	0.3	2	0.0174
3	5.0	0.3	3	0.0206
4	5.0	0.3	5	0.0340
5	3.0	0.3	7	0.0480
6	3.0–6.0	0.3	10	0.0580
7	3.0–7.0	0.3	15	0.0866
8	3.0–4.0	0.3	20	0.1243
9	3.6–5.0	0.3	25	0.1423

Summary.

Acetate in acetate, 25 min., 0.1250 gram cadmium.
Formate in formate, 20 min., 0.1938 gram cadmium.
Lactate in lactate, 20 min., 0.1314 gram cadmium.
Acetate in formate, 10 min., 0.1050 gram cadmium.
Formate in acetate, 30 min., 0.1852 gram cadmium.
Lactate in acetate, 10 min., 0.1011 gram cadmium.
Lactate in formate, 15 min., 0.1521 gram cadmium.
Formate in lactate, 20 min., 0.1275 gram cadmium.
Acetate in lactate, 15 min., 0.0866 gram cadmium.

As may be seen, the quantity of cadmium that will form an adhesive deposit varies very much with the different electrolytes as does also the rate of deposition.

The above work would seem to indicate that the deposits are finer and more adhesive when the solution is decidedly acid. On the other hand, if too much acid is used it is apparently almost impossible to deposit the last traces of the metal.

MT. HOLYOKE COLLEGE, SOUTH HADLEY, MASS.

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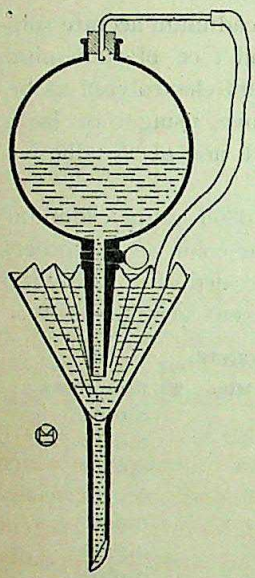
NOTES.

An Automatic Filter.—I have found the apparatus shown in the cut useful in filtering large amounts of solution from a precipitate of such a character that it passes readily through the stem of a separatory funnel. It is, of course, only a modification of the inverted flask principle, but it possesses the advantage that it can be refilled without moving or unclamping any large piece of glass apparatus. It can be made from apparatus always on hand in the laboratory.



To set it up, a separatory funnel as large as possible is mounted on a ring stand over a filter funnel containing a folded filter in such a manner that the stem of the separatory funnel is a little above the vertex of the paper. A tube passing through a one-hole rubber stopper in the top of the separatory funnel is brought down so that its outer end is held at the level at which it is desired to maintain the liquid in the filter funnel. When the separatory funnel is filled, the stopper put in and the stopcock opened, the solution runs into the lower funnel until it cuts off the air inlet through the tube to the upper vessel. When the level in the lower funnel has fallen sufficiently, a small amount of liquid is siphoned over into the upper one and the lower one fills up again.

The apparatus was used in filtering off barium carbonate from large amounts of solution in the preparation of inositol.

MARSTON L. HAMLIN.

COLUMBIA UNIVERSITY,
NEW YORK, N. Y.

A Rapid Filtering Funnel.—The ordinary funnels used in analytical work may be made to filter far more rapidly than usual—by deeply etching lines from a point below the apex of the funnel to points forming a ring about two-thirds of the way up the sides, in the following manner:

Coat the inside of the funnel with a layer of paraffin wax (containing a little turpentine or other agent to render the wax non-brittle) and allow part of the wax to run down into the tail and form a solid plug about 5 mm. below the apex of the funnel or well below the lowest point reached by the filter paper.

Scratch six or eight lines in the wax coating extending from the point *B*, to the wax plug at *A*, now fill the funnel to a point above *B* with hydro-

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fluoric acid and allow to stand twenty-five minutes; then pour out the acid into another funnel prepared as the first and so on until as many funnels have been prepared as required.

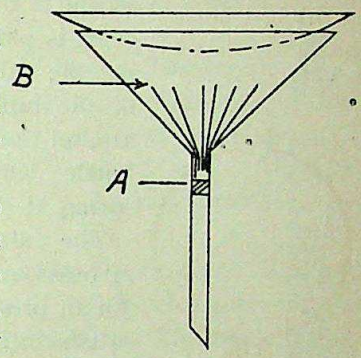

Fig. I

The funnel should be covered with a waxed beaker cover. The wax may be removed by hot water and the deeply etched grooves cleaned out with the point of a mechanic's scratch-awl or other suitable tool.

These grooves are not large enough to allow a filter paper to be broken by the stream from a wash bottle, but afford efficient channels for the filtrate to flow down.

The funnels may be used with the filter cone and are especially valuable in filtering gelatinous precipitates, alumina, etc. The speed of filtration is increased by this means to about two and a half times the normal rate for a funnel not so treated. H. SPURRIER.

DETROIT, MICH.

A Method of Filling Reagent Bottles.—In a chemical laboratory in which several hundred students are working, it is very desirable, especially from an economical standpoint, that each student fill his own desk reagent bottles. There is, however, a serious objection to having students, especially Freshmen, pour concentrated acids from heavy bottles. To obviate this difficulty the following apparatus was devized, in which the acids are forced from the bottles by means of air pressure.

The acid bottles are placed upon a glass-topped table, two feet above which runs a pipe connected with a source of air pressure (Fig. 1). From this pipe valves are suspended by means of rubber tubing. On pressing the lower end of the valve in the funnel *B*, the valve is opened and the air pressure forces the liquid from *C* into the receptacle. As soon as the valve is taken out of the funnel it closes again, and the air pressure is released from the bottle through the open funnel. The instantaneous release of the pressure prevents any dipping from *C*.

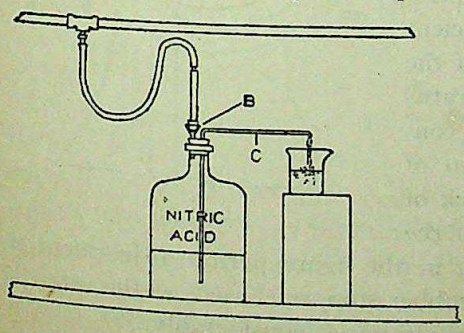

Fig. 1.

The details of the valve are shown in Fig. 2. Its essential parts are: The brass plunger *D*, provided with a nut *E*, the rubber stopper *F*, the rubber collar *G*, and the spring *H*. When the end of the valve is pressed

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against the funnel of the bottle, the plunger is forced upwards as a result of forcing the nut against the sides of the funnel. This permits the escape of the compressed air; the rubber stopper, however, is placed so near the nut that the act of pressing the valve down brings the rubber against the side of the funnel so tightly that the air cannot escape around the edges of the stopper but is forced into the bottle. On removing the valve from the funnel, the spring at once closes it by forcing the piston down.

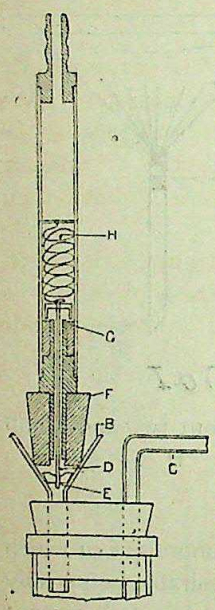

Fig. 2.

The valve is six inches long. The metal parts are of brass and were made by the University mechanic. An air pressure of about three pounds is found to work satisfactorily in this apparatus.

The above principle is particularly useful in drawing stock solutions. Barium chloride solutions, for example, are prepared by placing the weighed quantity of the salt in the bottle, adding warm water and shaking from time to time. A piece of muslin is fastened over the lower end of *C* (Fig. 1) so that reagent bottles may be filled as soon as the salt is dissolved, the necessity of filtering the solution by the usual slow process being thus obviated.

In forcing solutions from carboys in this manner, it was found that the pressure necessary in this case was sufficient to force the stopper from the neck of the carboy. To prevent this the apparatus shown in Fig. 3 was devized. It consists of three pieces of maple, two of which fit under the flange at the neck of the carboy, the third rests on top of the stopper. The thumb screws shown in the figure permit adjustment to different sized carboys. A conical rubber stopper is used, as the internal diameter of the necks of different carboys varies considerably.

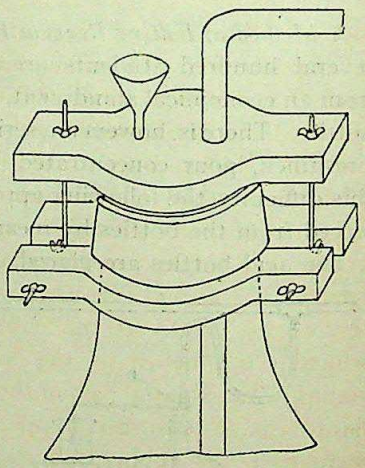
Fig. 3.

J. H. WALTON, JR.

A Hydrogen Sulfide Tap.—Not the least of the problems connected with the distribution of hydrogen sulfide gas to large classes in qualitative analysis is that of providing an outlet tap which cannot be left open by the student. In the author's laboratory, in which seven hundred students

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are studying qualitative analysis, many attempts were made to solve this difficulty before a satisfactory apparatus was devized. The apparatus described below is the result of several years' experience, and in its present form seems to be "fool-proof."

It is obvious that a satisfactory outlet tap should close automatically after the student is through using it. Certain types of mercury valves which are connected with the tap and close automatically as soon as the student is through with them are in use in some laboratories. These are usually made of glass, however, and since they are easily broken their use has been found impracticable.

The tap shown in Fig. 1 is essentially a strong spring pinch clamp, *A*, fastened to a board. By pushing the lever *B* (made of a piece of iron $^3/_8$ inch square) the clamp is opened, permitting the hydrogen sulfide to pass through the rubber tube *C*. The student attaches his glass delivery tube at *C*, pushes the lever until he has obtained sufficient hydrogen sulfide, then on releasing *B* the supply of gas is at once cut off. The rate of flow of gas is regulated by the screw pinchcock *D*.[1] Different kinds of rubber tubing have been used in this apparatus. It has been found, however, that a thick-walled gum tubing gives best service, for the usual grade of tubing employed for burners, etc., after being used a very few weeks, cracks at the point at which it is pinched by the spring clamp. An essential part of the apparatus is *E*, a rubber stopper cemented to the rubber tube. It rests on the board *F* and prevents the rubber tube from being pulled from its connection when a careless student pulls his glass delivery tube from the end of *C*. It has been found advizable to enclose the tap in a box, so that the student has access to the end of the lever and about two inches of the end of the rubber tube.

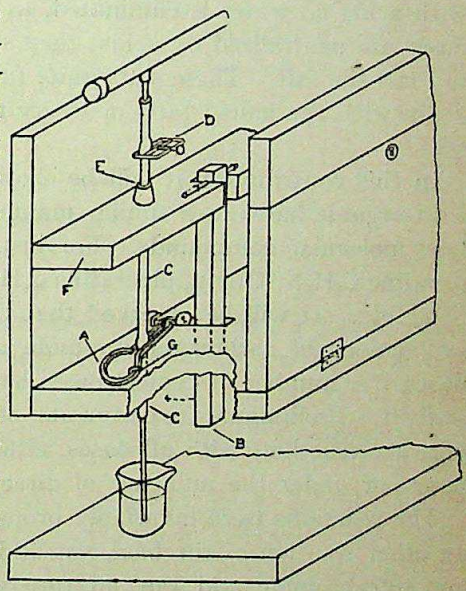

Fig. 1.

The spring clamps used are the strongest on the market. They must be renewed occasionally, but this is easily done if they are screwed down as shown in the figure at *G*.

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[1] A piece of glass, capillary tubing of very small bore is used for this purpose in many laboratories.—Editor.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

THE ACTION OF CARBON TETRABROMIDE ON ORGANIC BASES.

BY WILLIAM M. DEHN AND ALBERT H. DEWEY.

Received July 28, 1911.

Molecules of certain compounds exhibit a tendency to unite with molecules of other compounds without the formation of by-products. The resulting molecular aggregates or "molecular compounds" are true chemical compounds because, being of constant composition, they conform to the laws of definit and multiple proportions. In organic chemistry almost every group furnishes examples of molecular compounds. This property, however, is best exemplified with compounds containing cyanogen and basic nitrogen. Thus when the amines or the alkaloids react with acids no water is eliminated, as is the case usually when inorganic bases are neutralized by acids; they simply unite, molecule for molecule, to form the salt. These salts unite further with other compounds, especially with the haloid salts of heavy metals, to form the so-called double salts.

In this contribution it will be shown that carbon tetrabromide reacts with organic bases in a similar manner and that the initial products are true molecular compounds. For instance, quinoline yields $C_9H_7N.CBr_4$, pyridine $C_5H_5N.(CBr_4)_2$, piperidine $C_5H_{11}N.(CBr_4)_2$, ethylamine $(C_2H_5NH_2)_4$-CBr_4, etc. It will be observed that these compounds represent different proportions of carbon tetrabromide united with the respective organic bases. A number of typical bases have been studied and are herein described. Preliminary experiments on all types have been made and indicate reactions with all bases, either at ordinary or elevated temperatures, or under the influence of direct sunlight.

The reactions were invariably brought about in ether solution; usually an ether solution of the base was added to an ether solution of the carbon tetrabromide and the mixture was permitted to stand a number of hours or days. The best results were obtained when absolute ether was employed and all contact with moist air was avoided. Sometimes an immediate precipitation of crystals occurred; most often several hours or days were necessary to yield the crystals. Since both the organic bases and the carbon tetrabromide are soluble in ether, the formation of any crystals was an indication of a reaction, and its progress could be estimated by the rate of such precipitation. When the precipitation had progressed sufficiently, the ether was decanted and the precipitates were washed with anhydrous ether. They were then either analyzed directly or after recrystallizing from chloroform or other solvents.

Since, as will be shown below, hydrobromides of the respective bases

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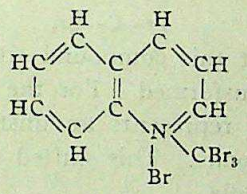
are the end-products of many of the reactions, or they were invariably obtained from the reaction products by treatment with water, the formation of these salts was an indication of the progress of the reaction, even when no precipitates were obtained from the ether solutions or when these precipitates represented mixtures difficult to separate.

A rational explanation of the mechanism of formation of the initial molecular aggregates and the salts of the bases is attended with great difficulty if a hypothesis of vaguely described "molecular valencies" is employed, or if the usually accepted ionic or kinetic hypotheses are resorted to.

Briefly, it may be stated that an hypothesis of "valencies of compounds" is so at variance with the conceptions of structure of organic compounds that it can and must be dispensed with. Therefore we are concerned most largely with the adequateness of the ionic and kinetic hypotheses.

Let us consider, by way of illustration, the formation of *quinoline carbon tetrabromide* and assume its structure to be

(1)



The *ionic* and also the *kinetic* hypotheses would require a *preliminary dissociation* of the carbon tetrabromide as indicated in the equation,

(2) $$CBr_4 \longrightarrow CBr_3 + Br,$$

and a subsequent addition of these parts to the trivalent nitrogen atom, yielding the structure shown above.

However, (1) since the reactions are brought about in anhydrous ether, itself a non-electrolyzing medium, (2) since the evident rates of reaction are different, and (3) since sunlight is an accelerating agent, the conclusion is inevitable that preliminary ionic or kinetic dissociation of the carbon tetrabromide is not the *sine qua non* of the reaction. If the reactions were dependent upon this dissociation of carbon tetrabromide, then not only would reactions with all organic bases result but the *rates* of reaction would be equal and, by analogy with known ionic reactions, these rates would be practically instantaneous. However, easily followed differences of reactions are observable, and the rates often are extended over weeks of time. Therefore the reactions are not dependent upon a state of *constant dissociation of the carbon tetrabromide.*

Let us then look to the bases themselves for an explanation of the reactions. Except in cases of the quaternary compounds, the nitrogen organic bases are weak; in fact they differ but little from ammonia itself in basic properties, hence wide variations of reaction would not be ex-

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pected if relative basic properties were the cause of variation. However, wide variations of reactions are observed and therefore degrees of ionization of the bases, or relative kinetic dissociation of the same, are not to be assigned as the cause of these variations of reactions.

We must then turn to other possibilities of the case. It must be remembered that most organic bases contain atoms of nitrogen in the trivalent condition. These atoms are potentially pentavalent, and therefore all of these compounds are potentially reactive; in other words, the two "latent," "residual," or "partial" valencies present the possibilities of reaction, and reactions will result if other causes do not supervene. Bromine likewise has residual valencies and if a molecule of carbon tetrabromide is brought within the sphere of reaction of a molecule of an organic base it may be assumed that there is first a *coalescence*,[1] due to the residual valencies of the nitrogen and the bromine, which may be represented as follows:

(3)
```
R—N—H2
  ||
Br—C—Br3
```

It may be assumed that this compound either is reversibly dissociated or is progressively transformed. For the reason that in the above formula trivalent bromine represents an unstable state, we can easily conceive of a shifting of bonds. This shifted state of the valencies may be represented by the formula

(4)
```
R—N—H2
  |\
  | CBr3 ,
  Br
```

a compound analogous in composition and stability to the salts of the base.

In consideration of the two molar aggregates, (3) and (4), there can be little doubt but that the latter correctly represents the structure of the stable end-product, for we arrive at this same structure if we proceed on a kinetic, an ionic, or the above-described coalescent basis. Only the initial coalescent molecule (3) requires proof.

The fact that the kinetic and the ionic hypotheses are themselves inadequate to account for the end-product is sufficient to justify some other hypothesis. The above-described *coalescent hypothesis*, employing as it does only the usually accepted assumptions of the science, is offered as an explanation. However, some evidence apparently confirming the assumption is gathered. Sunlight is necessary for the starting, progress, and completion of some of these reactions. Cases of no reaction, when the ether solutions have been preserved for days in darkness,[2] have given an immediate precipitate when brought into direct sunlight. This ac-

[1] See *Am. Chem. J.*, 40, 93.

[2] See Pyridine, p. 1594.

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celerating effect of sunlight may be accounted for in two ways: either the actinic rays produce a kinetic dissociation as represented by equation (2) above, or these rays *promote the shifting of bonds* as represented by the transformation of (3) to (4). That the latter is more probable is indicated by the fact that *heat*, the specific agent in kinetic dissociations, does not promote some of these reactions, whereas sunlight does. The transverse ether vibrations of light evidently produce effects different from those produced by heat vibrations.

With pyridine and piperidine, one molecule of the base unites with two molecules of carbon tetrabromide. That these two molecules of carbon tetrabromide are held by the base with different degrees of tenacity and that they are differently united in the molar aggregate is evidenced by two different lines of observations. First, vapor pressure curves indicate a dissociation of one molecule of carbon tetrabromide below 100° and of the second molecule between 100° and 210°. Second, when decomposed by water the complex compound yields products in accordance with the equation

(5) $C_5H_7N.(CBr_4)_2 + 2H_2O \longrightarrow CBr_4 + CO_2 + 3HBr + C_5H_7N.HBr.$

Here one molecule of carbon tetrabromide is liberated as such and the other molecule is decomposed into carbon dioxide, water, and hydrobromic acid. By analogy with (3) and (4) above we may, therefore, assume the following structures for *pyridine dicarbontetrabromide*:

(6)
```
C5H5N.CBr3                      C5H5N.CBr3
|                    ⟶          |
Br :: Br . CBr3                 Br—Br—CBr3
```

(7)
```
C5H5N.Br                        C5H5N.Br
|                               |
Br2C—Br :: Br.CBr3   ⟶          Br2—C—Br—CBr3
                                |
                                Br
```

If either (6) or (7) is the correct formula it is impossible at present to indicate the more probable one. In one case the trivalent bromine atom is assumed to be united to *nitrogen*; in the other case, to the *methane carbon* atom.

From equation (5) above it is evident that a hydrobromide salt of the base is formed when those compounds containing "carbon tetrabromide of crystallization" are treated with water. It was found that these salts were always produced when moist ether was employed, also sometimes even when anhydrous conditions were observed; that is, primary and secondary amines yield salts in the absence of water in accordance with the following equations:

(8)
```
R—NH2
|\
|  CBr3   ⟶   R—NH  +  HBr
Br              |
                CBr3
```

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(9) $$R—NH_2 + HBr \longrightarrow R—NH_2HBr.$$

Tertiary bases, containing, as they do, no N-hydrogen, do not yield salts except in presence of water. In cases of primary and secondary amines these salts are more often the only crystallin products. This ether solution method is, in many cases, the best method of preparation of pure hydrobromides of organic bases, hence a number of new hydrobromides have been contributed. For the purpose of identification, a number of bromoaurates also are contributed.

The mechanism of reaction of water on the carbon tetrabromides may be indicated as follows:

(10) $$R—NH_2=(CBr_3)Br=OH_2 \longrightarrow R—NH_2 : (CBr_3)Br : H(OH) \longrightarrow R—NH_2HBr + CBr_3OH.$$

The hypothetical substance *tribromocarbinol* may be decomposed as follows:

(11) $$CBr_3OH + H_2O \longrightarrow 3HBr + CO_2.$$

Since four molecules of hydrobromic acid were formed, the resulting aqueous solutions were usually *acid*. Sometimes, however, the solutions were *neutral* or *alkaline*, thus indicating an incomplete reaction according to (10). In fact, since carbon tetrabromide was obtained in the aqueous solution, the effect of hot water was largely in accordance with the equation

(12) $$R—NH_2CBr_3Br \longrightarrow R—NH_2 + CBr_4.$$

Preparation of the Sodium Hypobromite.—To prepare a sodium hypobromite solution of maximum concentration, the method previously described by one of us[1] was employed.

Methods of Preparation of Carbon Tetrabromide.—(*a*) The method previously suggested by one of us[2] was found to be easy and economical. Bromoform was placed in stout bottles with an excess of sodium hypobromite solution and shaken either occasionally by hand or constantly by some convenient shaking device. When the liquid bromoform was transformed to a solid mass of crystals of carbon tetrabromide, most of the clear supernatant hypobromite solution was removed by decantation and the remaining mixture was subjected to steam distillation. Pure carbon tetrabromide passed over and was separated from the water and dried on filter paper or clay plates, or better the mass of wet crystals was melted and resolidified, when the supernatant water could easily be poured off and the carbon tetrabromide dried by filter paper used as a blotter.

(*b*) In a convenient sized flask, bleaching powder is treated with an excess of a solution of sodium bromide. The spent sodium hypobromite

[1] THIS JOURNAL, 31, 526.

[2] *Ibid.* 31, 1227; cf. *Ann.*, 167, 174; *Ibid.*, 275, 149; *Soc.*, 65, 264.

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solution used above, containing as it does most of the bromine in the form of sodium bromide, is conveniently and economically employed. When the bleaching powder and the sodium bromide are brought into contact a yellow solution of hypobromite is formed. This is then treated with acetone in quantities not quite sufficient to discharge the yellow color. This mixture is permitted to stand until the next day, being shaken occasionally if convenient. Finally the mixture is subjected to steam distillation. From 20 g. of acetone 62 g. of CBr_4, or 53 per cent., were obtained.

Preparation of Solutions.—In the earlier experiments ordinary ether was used, but mixtures of varied composition were formed. It was found that these mixtures resulted from the action of water on the carbon tetrabromide compounds of the bases, which were first formed. When absolute ether was employed, no such difficulties were encountered. If necessary, the ether solution of carbon tetrabromide was dried with calcium chloride before adding to the ether solution of the base. The action of moist air was avoided in the removal of the crystals and in the subsequent treatment of the solutions.

Piperidine.—When equimolecular quantities of piperidine and carbon tetrabromide in dry ether solutions were mixed, an immediate, white, flaky precipitate was formed. This precipitate increased steadily on standing and finally yielded beautiful prismatic needles melting at 148°. Coarse needles were easily obtained by heating the ether solutions in a sealed tube.

Calculated for $C_5H_{11}N.(CBr_4)_2$: Br, 85.42; C, 11.23; H, 1.48; N, 1.87.
Found: Br, 85.33; C, 11.13; H, 1.26; N, 2.17.

Piperidine dicarbontetrabromide is decomposed by heat alone in accordance with the equations:

(13) $$C_5H_{11}N.(CBr_4)_2 \longrightarrow C_5H_{11}N.CBr_4 + CBr_4$$

(14) $$C_5H_{11}N.(CBr_4)_2 \longrightarrow C_5H_{11}N + 2CBr_4.$$

When water is present the above decompositions and the following one take place:

(15) $$C_5H_{11}N.(CBr)_2 + 2H_2O \longrightarrow C_5H_{11}N.HBr + CBr_4 + 3HBr + CO_2.$$

Equation (14) yields an alkaline end reaction toward litmus; equation (15), an acid end reaction; a proper combination of (14) and (15), a neutral end reaction. In different decompositions by cold and hot water these various conditions of end reaction were observed; however, usually an alkaline end reaction was observed, showing that there is a preponderance of reaction (14). The carbon tetrabromide was identified by its melting point and other properties; the hydrobromic acid, by the acidity of the aqueous solution; the carbon dioxide, by passing the aqueous decomposition product into lime water; the hydrobromide of piperidine,

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by evaporating the solution and recrystallizing the residue from absolute alcohol, when it was found to darken and melt at 238°–239°.[1]

Calculated for $C_5H_{11}N.HBr$: C, 36.14; H, 7.29; Br, 48.14.
Found: C, 36.55; H, 8.03; Br, 48.21.

Bromoaurate, dark, red-brown needles melting at 242°.

Calculated for $C_5H_{11}N.HBr.AuBr_3$: Au, 32.73.
Found: Au, 32.61.

Pyridine.—When equimolecular quantities of pyridine and carbon tetrabromide were brought together in dry ether solution, they yielded a voluminous crop of iridescent crystals which were easily recrystallized from chloroform. A solution of the two reacting substances could be preserved for hours or days in the dark without precipitating; in the direct sunlight the precipitation was immediate. The crystals darken at 155° and melt at 218–220°. By the pycnometer method with benzene, the specific gravity was found to be 2.70 at 21°.

Calculated for $C_5H_5N.(CBr_4)_2$: C, 11.31; H, 0.68; N, 1.89; Br, 86.12.
Found: C, 11.30; H, 1.04; N, 2.01; Br, 85.89.

Pyridine dicarbontetrabromide is decomposed by heat alone, yielding the first molecule of carbon tetrabromide below 100° and the second molecule near its melting point. The reaction is at best difficultly reversible, for after heating the vapor pressure at ordinary temperature is much greater than the original pressure at ordinary temperature.

VAPOR PRESSURES[2] OF PYRIDINE DICARBONTETRABROMIDE.

Temperature.	1st sample.	2nd sample.	Temperature.	1st sample.	2nd sample.
26	..	11	107	87	...
28	..	14	111	...	242
32	..	21	113	101	...
36	..	24	115	...	255
42	..	31	116	115	...
46	..	39	120	...	281
47	..	61	126	146	...
52	..	65	131	167	...
55	8	..	135	...	344
60	..	87	136	187	...
62	..	99	141	193	...
65	..	104	150	...	410
66	12	...	155	216	...
72	..	128	160	...	465
76	..	140	164	252	...
79	35	...	170	...	520
81	..	149	175	334	...
82	..	156	190	434	...
91	..	203	198	650	...
92	58	...	208	981	...
97	..	215	212	1381	...
106	78	...			

[1] Bischoff gives melting point at 235°, *Ber.*, 31, 2841; Fock, *Ber.*, 32, 1409.
[2] For method used see THIS JOURNAL, 29, 1052–65.

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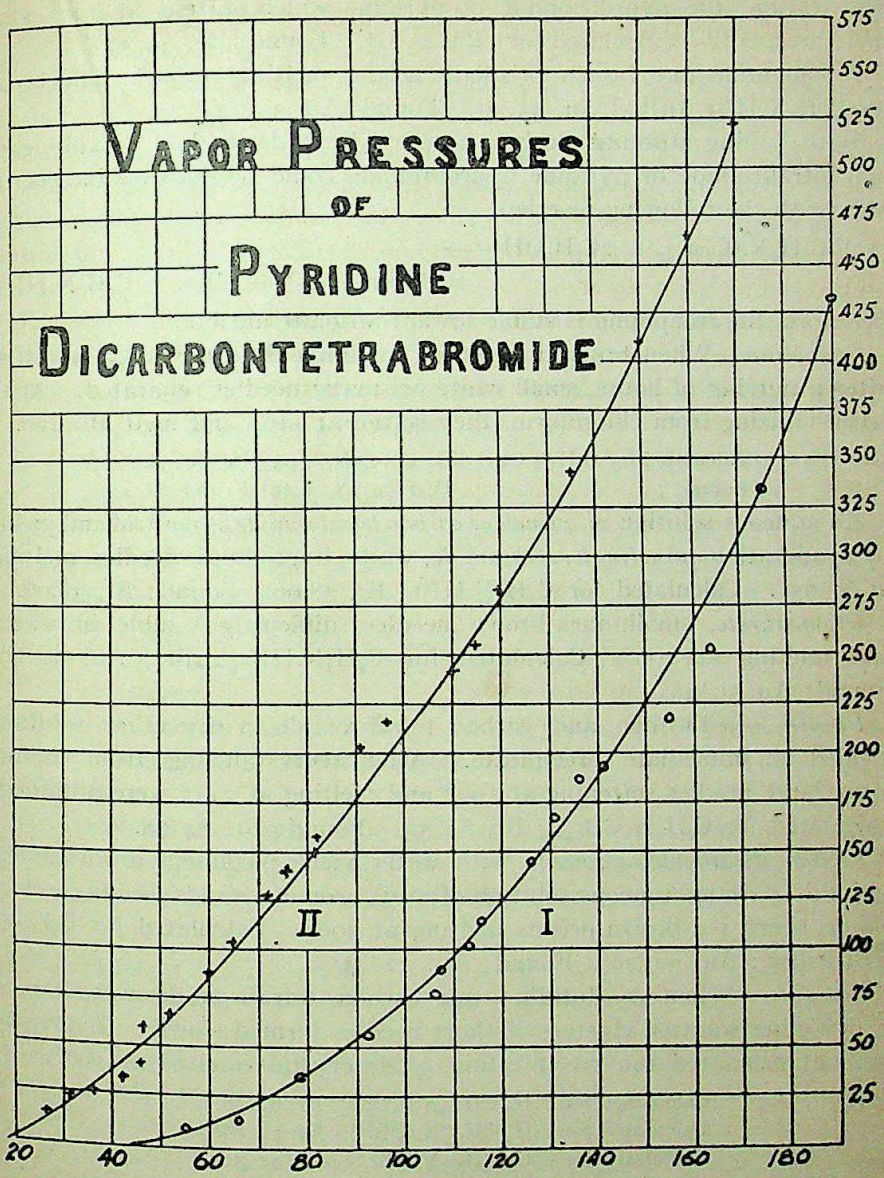

Sample (1) was dried at ordinary temperature for a number of days in a desiccator and sample (2) was used as soon as freed from solvent. With water it decomposes in a manner analogous to piperidine dicarbontetrabromide, yielding, however, an acid end reaction; hence the main reaction is

(16) $C_5H_5N.(CBr_4)_2 + 2H_2O \longrightarrow C_5H_5N.HBr + 3HBr + CO_2 + CBr_4$.

The cold aqueous solution yielded bubbles of carbon dioxide and, by

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evaporation, the hydrobromide of pyridine which softens at 200° and melts at 213°.[1] Calculated for: Br, 49.95. Found: Br, 49.57.

Bromoaurate, fine, brown, prismatic needles melting at 319°. Calculated for $C_5H_5N.HBr.AuBr_3$: Au, 33.03. Found: Au, 33.15.

With boiling absolute alcohol, no ethyl bromide, carbon dioxide, carbon tetrabromide or pyridine hydrobromide could be detected in accordance with the following reaction:

$$(17)\quad C_5H_5N.(CBr_4)_2 + 2C_2H_5OH \longrightarrow 2C_2H_5Br + CO_2 + CBr_4 + C_5H_5N.HBr;$$

therefore, the compound is stable toward absolute alcohol.

Quinoline.—When brought together, an immediate turbidity resulted; after a number of hours, small white prismatic needles separated. After recrystallizing from chloroform, they soften at 110° and melt at 142°.

Calculated for $C_9H_7N.CBr_4$:	H, 1.55; N, 3.04; Br, 69.38.
Found:	H, 1.74; N, 3.20; Br, 69.23.

An aqueous solution of *quinoline carbon tetrabromide* is neutral and yields by evaporation *quinoline hydrobromide*, white, hygroscopic needles, melting at 62–65°. Calculated for $C_9H_7N.HBr$: Br, 38.06. Found: Br, 38.06.

Bromoaurate, small, dark brown needles, difficultly soluble in water and melting at 209°. Calculated for $C_9H_7N.HBr.AuBr_3$: Au, 30.49. Found: Au, 30.48.

Picoline.—α-Picoline and carbon tetrabromide in dry ether solution yielded an immediate precipitate. After recrystallizing from chloroform, large needles softening at 190° and melting at 214° were obtained. Calculated for $C_6H_7N(CBr_4)_2$: Br, 84.52. Found: Br, 84.78.

Picoline dicarbontetrabromide, with water, yields picoline hydrobromide,[2] and this, with an aqueous solution of auric bromide, yields *picoline bromoaurate*, short, red-brown prisms melting at 209°. Calculated for $C_6H_7N.HBr.AuBr_3$: Au, 32.29. Found: Au, 32.25.

Lutidine.—When α,α-lutidine and carbon tetrabromide were mixed in dry ether solution clusters of short needles formed slowly. Evidently sunlight promoted the precipitation. The crystals melted at 106°.

Calculated for $C_5H_3(CH_3)_2N.(CBr_4)_4$:	Br, 82.98.
Calculated for $C_5H_3(CH_3)_2N.(CBr_4)$:	Br, 72.86.
Calculated for $C_6H_3(CH_3)_2N.HBr$	Br, 42.51.
Found:	Br, 69.40.

Evidently *lutidine carbon tetrabromide*, or a mixture of dicarbontetrabromide with *lutidine hydrobromide* was formed. The latter was obtained from the aqueous solution as white hygroscopic needles melting, not sharply, at 114°. Found: Br, 42.64.

Its *bromoaurate* consisted of dark brown needles melting at 180° and

[1] Trowbridge gives the melting point at 200°; THIS JOURNAL, 21, 67.

[2] Murrill, THIS JOURNAL, 21, 842; Ramsay, *Phil. Mag.*, [5] 2, 271.

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easily soluble in water and alcohol. Calculated for $C_5H_3(CH_3)_2N.HBr.AuBr_3$: Au, 31.55. Found: Au, 31.70.

Phenylhydrazine.—Equimolecular quantities of phenylhydrazine and carbon tetrabromide in dry ether gave an immediate precipitate of mother-of-pearl leaflets and an evolution of nitrogen. The ether solution, distilled first directly and then with steam, yielded bromoform, carbon tetrabromide, and a yellow residue. The leaflets melted sharply at 210°. Calculated for $C_6H_5N_2H_3.HBr$: N, 14.83; Br, 42.29. Found: N, 14.74; Br, 42.48.

The substance was phenylhydrazine hydrobromide[1] and the main reaction evidently was as follows:

$$(18)\ C_6H_5NHNH_2 + CBr_4 \longrightarrow C_6H_5NHNH_2.HBr + CHBr_3 + N_2.$$

This reaction will be investigated further.

Benzylamine.—Equimolecular quantities of benzylamine and carbon tetrabromide gave an immediate and voluminous precipitate of benzylamine hydrobromide, appearing as beautiful, white, glistening leaflets, melting at 204°.[2] When heated with water, some undissolved carbon tetrabromide appeared, indicating its somewhat impure form.

Calculated for $C_6H_5CH_2NH_2.HBr$:	N, 7.45; Br, 42.51.
Calculated for $(C_6H_5CH_2NH_2)_4.CBr_4$:	N, 7.37; Br, 42.06.
Found:	N, 8.17; Br, 40.70.

The *bromoaurate* consists of long, fan-like, brownish red flakes, melting at 178°. Calculated for $C_6H_5CH_2NH_2.HBr.AuBr_3$: Au, 31.35. Found: Au, 31.43.

Diisoamylamine.—Equimolecular quantities of the two substances yielded immediately beautiful feathery crystals. After a few days a solid mass of crystals, so compact that the ether would not flow off, was formed.

Calculated for $(C_5H_{11})_2NH.HBr$:	C, 50.39; H, 10.15; N, 5.89; Br, 33.56.
Calculated for $[(C_5H_{11})_2NH.]_4CBr_4$:	C, 51.22; H, 9.65; N, 5.83; Br, 33.28.
Found:	C, 49.69; H, 9.74; N, 6.45; Br, 33.61.

Dipropylamine.—Needles melting at 144.5° were formed immediately. Analyses indicated that the crystals were a mixture of the hydrobromide and the carbon tetrabromide derivative.

Ethylamine.—An immediate precipitate of beautiful, white, feathery crystals resulted. These needles were found to be a mixture of two compounds. One, easily soluble in water and insoluble in chloroform, melted

[1] Two hydrobromides are described: $C_6H_5N_2H_3.HBr$ (Balbiano, *Gazz. chim. ital.*, 16, 138), needles, m. p. 204° (Broche, *J. prakt. Chem.*, 50, 113); $(C_6H_5N_2H_3)_2.HBr$ (Allain le Cann, *Compt. rend.*, 129, 105) decomposing and melting at 195°. The latter is prepared by a method somewhat analogous to the above; le Cann treated phenylhydrazine with ethyl bromide in ether solution. Broche's preparation, melting at 204°, is evidently less pure than the above, melting at 210°.

[2] Bischoff gives m. p. at 206°, *Ber.*, 30, 3170.

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at 157°. It proved to be *ethylamine hydrobromide*. Calculated for $C_2H_5NH_2.HBr$: Br, 62.59. Found: Br, 62.43.

Bromoaurate, coarse, red-brown prisms melting at 190°. Calculated for $C_2H_5NH_2.HBr.AuBr_3$: Au, 35.03. Found: Au, 34.98.

The second compound referred to is easily soluble in chloroform; on treating with water, insoluble carbon tetrabromide was formed. From boiling chloroform beautiful prismatic needles melting at 150° were obtained. Calculated for $(C_2H_5NH_2)_4CBr_4$: Br, 62.44. Found: Br, 62.39.

These compounds will be more closely investigated.

SEATTLE, WASHINGTON.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

THE ACTION OF DIIODOACETYLENE ON ORGANIC BASES.

BY WILLIAM M. DEHN.

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Diiodoacetylene was first prepared by Berend[1] from silver acetylide and iodine in ether solution. Biltz[2] prepared it from calcium carbide and iodine in potassium iodide solution. Nef[3] prepared it from tetraiodoethylene and acetylene diiodide[4] by treatment with alkali alcoholates.

New Method of Preparation.—The following excels the above methods not only in the ease of preparation but also in the quality and quantity of the yields. Water is admitted from a dropping funnel to a flask containing calcium carbide, at such a rate that a steady stream of gas is generated. The acetylene is conducted into a flask containing a solution of potassium iodide and carrying a dropping funnel and an exit tube.[5] A solution of sodium hypochlorite[6] or sodium hypobromite,[7] preferably the former,[8] is admitted a drop at a time. By reaction with potassium iodide, the hypohalite yields a yellow or brown-red colored solution and this, with the acetylene, immediately forms a beautiful flocculent precipitate of the diiodoacetylene. The precipitate increases in volume until the potassium iodide is exhausted and finally forms, during the pas-

[1] *Ann.*, 135, 256; cf. Baeyer, *Ber.*, 18, 2274; also Nef, *Ann.*, 298, 343.

[2] *Ber.*, 30, 1202; cf. G. de Chalmot, *Am. Chem. J.*, 19, 877.

[3] *Ann.*, 298, 341.

[4] *Ibid.*, 298, 342.

[5] The unchanged excess of acetylene may be passed into a gas reservoir and later passed again through the solution.

[6] This is best prepared by dropping concentrated hydrochloric acid into a flask containing potassium permanganate and passing the chlorine into a moderately concentrated solution of sodium hydroxide.

[7] For the best method of preparing sodium hypobromite, see THIS JOURNAL, 33, 526.

[8] With sodium hypochlorite, acetylene does not precipitate at all; with sodium hypobromite it precipitates "an oil." G. de Chalmot, *Am. Chem. J.*, 19, 878.

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sage of the acetylene, a white mass, conpletely filling the solution, but settling on standing. When the solution of potassium iodide loses its property of coloring by the addition of hypohalite or when an excess of acetylene has passed through the mixture, the white crystals are filtered from the solution, washed with water and dried on clay plates. From 100 g. of potassium iodide, 78 g. of crystals melting at 79° were obtained. The theoretical yield was 89 g. By dissolving in low-boiling ligroin,[1] drying with calcium chloride, and cooling with ice-water, crystals melting at 81° were obtained. Calculated for C_2I_2: I, 91.36. Found: I, 91.33.

The reactions involved in the preparation of diiodoacetylene are:

$$CaC + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2;$$
$$KI + NaOCl \longrightarrow KCl + NaOI;$$
$$2NaOI + C_2H_2 \longrightarrow 2NaOH + C_2I_2.$$

Since sodium hypoiodite is quickly decomposed in accordance with the reactions

$$3NaOI \longrightarrow 2NaI + NaIO_3,$$
$$NaOI + 3NaOCl + NaOH + H_2O \longrightarrow 3NaCl + H_3Na_2IO_6,$$

some of the iodine is not converted into diiodoacetylene. Furthermore, some of the latter is also lost owing to its being volatil and also somewhat soluble in water. However, since diiodoacetylene is directly obtainable from acetylene in the manner described and in 80–90 per cent. yields, the advantages of this method of preparation are evident.

It was anticipated that diiodoacetylene is more reactive than is indicated by the reactions found in the literature. From experiments herewith contributed and from indications of other experiments under way, this surmize has been found to be correct. Diiodoacetylene reacts with organic bases in a manner analogous to the reaction of carbon tetrabromide on organic bases, yielding, most commonly, an aggregate of the base with two molecules of the diiodoacetylene.

Triethylamine and Diiodoacetylene.—When concentrated ether solutions of the two substances in molecular proportions were brought together, white feathery clusters of needles were formed after some time. On filtering, washing with ether, and drying on a clay plate, the crystals became light yellow in color. The substance darkens at 97°, blackens at 104°, and melts at 115°. It is quite readily volatil and somewhat soluble in water with a neutral reaction.

Calculated for $(C_2H_5)_3N(C_2I_2)_2$: N, 2.13; I, 77.29.
Found: N, 2.20; I, 77.13.

The decomposition of *triethylamine diiodoacetylene* has not been studied.

Dipropylamine and Diiodoacetylene.—An ether solution of the sub-

[1] Biltz, *Ber.*, 30, 1203. Nef, *Ann.*, 298, 344.

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stances in molecular proportions was prepared. The solution became red-violet in color and then long needles separated. They melted sharply at 160°.

Calculated for $(C_8H_7)_2NH(C_2I_2)_2$: N, 2.13; I, 77.99.
Found: N, 2.23; I, 77.19.

Piperidine and Diiodoacetylene.—When the two substances were brought together without the use of a solvent, they reacted with explosive violence and yielded a black solid mass. In ordinary ether solution the mixture yielded first an amber-colored solution, then a violet solution, and finally precipitated a gummy mass. In anhydrous ether solution, colorless needles, darkening at 117° and melting at 161°, were obtained. Calculated for $C_5H_{11}N(C_2I_2)_2$: I, 79.23. Found: I, 79.62.

Phenylhydrazine and Diiodoacetylene.—It was found that phenylhydrazine reacted with diiodoacetylene in an *anomalous* manner. Products thus far isolated are two hydroiodides of phenylhydrazine, phenylacetylene iodide, and elementary nitrogen.

When equimolecular quantities of phenylhydrazine and diiodoacetylene were dissolved in a small quantity of ether and the mixture was permitted to stand for a few hours, the color of the solution changed through light yellow and amber to dark red-brown, nitrogen was evolved and a matted mass of white crystals was obtained. The yield was greatly increased when two molecules of phenylhydrazine reacted with one molecule of diiodoacetylene. On filtering and recrystallizing from glacial acetic acid, needles of a beautiful luster were obtained.

Calculated for $(C_6H_5N_2H_3)_2HI$: C, 41.85; H, 4.98; N, 16.29; I, 36.88.
Found: C, 41.76; H, 4.70; N, 16.30; I, 36.79.

This *hydriodide of phenylhydrazine* melts with decomposition at about 128° and changes on standing in sunlight or on heating to the form of salt described below.

When the reaction mixture of phenylhydrazine and diiodoacetylene, prepared as described above and containing the needles, is permitted to stand for a number of days, or better, is heated for a few hours on the water bath under a return condenser, much nitrogen is evolved and the needles were replaced by a lesser volume of scale-like crystals. After filtering, washing with ether, and recrystallizing from glacial acetic acid, flaky mother-of-pearl crystals were obtained.

Calculated for $C_6H_5N_2H_3.HI$: N, 11.87; I, 53.79.
Found: N, 11.57; I, 53.64.

This *hydriodide of phenylhydrazine* darkens at 270° but does not melt at 300°. When 39 g. of C_2I_2 and 31 g. of $C_6H_5N_2H_3$ were used, 24 g. of $C_6H_5N_2H_3HI$ or $^3/_4$ mol. was obtained.

When 7 g. of C_2I_2 and 5.5 g. of $C_5H_5N_2H_3$ reacted, 750 cc. of nitrogen were evolved; this is equal to 57 per cent. of the total nitrogen.

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The ether solution was evaporated and a red oil of a peculiar odor was obtained. It was fractionated *in vacuo*. The larger fraction boiled at 144° and 26 mm. A number of analyses indicated that the oil is a mixture, approximating the percentages of composition of $C_6H_5C \equiv CI$; however, since all the products cannot be accounted for by an equation, such as:

$$2C_6H_5NHNH_2 + C_2I_2 \longrightarrow C_6H_5NHNH_2HI + C_6H_5C \equiv CI + N_2 + H_2,$$

other experiments must be made.

Other bases than the above-mentioned react with diiodoacetylene in ether solution and give well characterized crystallin products. These will be discussed in a future contribution.

SEATTLE, WASHINGTON.

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FASTING STUDIES: IV (STUDIES ON WATER DRINKING: VII). ON THE ALLANTOIN AND PURINE EXCRETION OF FASTING DOGS.

BY S. R. WREATH AND P. B. HAWK.

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Introduction.

The occurrence of allantoin as a urinary constituent was first demonstrated by Wöhler.[1] He found it to be present in the urine of suckling calves in sufficient quantity to separate out in crystallin form. The role played by allantoin in the metabolic processes of the animal organism, however, did not receive serious attention until about 50 years after Wöhler had made his pioneer observation. In fact for years it was believed that allantoin was confined, as an excretory product, to the urine of infants and the young of certain species of lower animals, among them the calf, as already mentioned.

It was early known, of course, that allantoin could be produced *in vitro* by the oxidation of uric acid. With this relation in mind, Wöhler and Frerichs[2] fed uric acid to dogs and rabbits as well as to men and searched for allantoin in the urine of the subjects. They were unsuccessful in their attempts to isolate the substance and consequently came to the conclusion that the uric acid which they had fed had undergone a profound oxidation in the animal body and that the final oxidation products were unknown substances below the allantoin stage. Several years later Neubauer[3] likewise made an unsuccessful attempt to demonstrate the presence of allantoin in the urine of rabbits after uric acid

[1] Wöhler, *Ann.*, **70**, 229 (1849).
[2] *Ann.*, **65**, 335 (1848).
[3] *Ibid.*, **99**, 217 (1856).

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feeding. Finally, in 1876, Salkowski[1] isolated fairly large quantities of allantoin from the urine of dogs which had been fed uric acid, and Minkowski[2] later confirmed this observation.

Our knowledge regarding the metabolic cycle of which allantoin is the end product has been greatly advanced through the investigations of Mendel[3] and his associates coupled with the work of Cohn,[4] Salkowski,[5] and Swain.[6] These investigators have demonstrated beyond question that an increased output of allantoin follows the introduction not only of uric acid but of purine derivatives such as free purine bases or the nucleic acids or their salts into the organism of the cat or dog. More recently Wiechowski[7] has secured allantoin as an oxidation product of uric acid through the enzymic power of extracts of the liver of the dog and the kidney of the ox. The yield of allantoin was nearly quantitative in these tests. Furthermore, Minkowski[8] and Paduschka[9] have shown that allantoin ingested by dogs may be obtained unchanged and practically quantitatively in the urine. This finding is further emphasized through the recent report of Schittenhelm and Wiener,[10] to the effect that 30 per cent. of the total quantity of allantoin ingested by human subjects may be obtained in the urine. These experiments just mentioned would seem to indicate clearly that we may with justice consider allantoin as an end-product of the oxidation of purine substances, at least in the human organism and in that of the dog. The finding of allantoin in the urine of fasting dogs by Underhill and Kleiner[11] and by Schittenhelm[12] and Wiechowski[13] strengthened the claim of allantoin to consideration as an end-product of purine metabolism. The uncertainty which formerly existed as to the normal occurrence of allantoin has been entirely dissipated through the interesting series of experiments by Wiechowski,[14] who has demonstrated the presence of allantoin in the

[1] *Ber.*, 9, 719 (1876).

[2] *Arch. exp. Path. Pharm.*, 41, 398 (1898).

[3] Mendel and Brown, *Am. J. Physiol.*, 3, 261 (1900). Mendel and Jackson, *Ibid.*, 4, 163 (1900). Mendel, Underhill and White, *Ibid.*, 8, 377 (1902–3). Mendel and White, *Ibid.*, 12, 85 (1904–5).

[4] *Z. physiol. Chem.*, 25, 507 (1898).

[5] *Centr. Med. Wiss.*, 929 (1898).

[6] *Am. J. Physiol.*, 6, 38 (1901).

[7] Hofmeister's *Beitr.*, 4, 295 (1907).

[8] *Arch. exp. Path.*, 41, 375 (1898).

[9] *Ibid.*, 44, 19 (1900).

[10] *Z. physiol. Chem.*, 63, 283 (1909).

[11] *J. Biol. Chem.*, 4, 165 (1908).

[12] *Z. physiol. Chem.*, 62, 80 (1909).

[13] Hofmeister's *Beitr.*, 11, 109 (1908).

[14] Hofmeister's *Beitr.*, 11, 109 (1908); *Arch. exp. Path. Pharm.*, 60, 185 (1909); *Biochem. Z.*, 19, 368 (1909.)

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urine of the dog, rabbit, cat, monkey, horse and man. This author has likewise elaborated a method for the determination of allantoin which is probably far more accurate than any method previously in vogue for this purpose.

Salkowski[1] has found allantoin to be present in the urine of the cow, whereas Swain[2] has isolated it from coyote urine, the latter observation having been very recently verified by Hunter and Givens.[3] The finding of allantoin in monkey urine has been verified by Wells.[4] According to Wiechowski allantoin is the only oxidation product of uric acid which appears in the urine following the subcutaneous injection of uric acid. In the case of rabbits, from 56.4 per cent. to 92 per cent. of the allantoin-equivalent of the uric acid injected was recovered in the urine.

Certain experiments of Abderhalden, London and Schittenhelm[5] are of interest in connection with nuclein metabolism. They worked upon dogs after the establishment of the Eck fistula.[6] They found that the elimination of the liver function by this means had no influence upon the decomposition of nucleic acid and the subsequent deamidation and oxidation of the purine bases. There was, however, a disturbance in the transformation of uric acid into allantoin, thus indicating a diminution in the uricolytic function of the liver. The following distribution of purine nitrogen was noted in Eck fistula dogs as compared with normal animals:

	Allantoin. Per cent.	Purine bases Per cent.	Uric acid. Per cent.
Normal	94–97	1–2	2–4
Eck fistula	74–87	1–2.5	12–25

It is now generally believed that allantoin is the principal end-product of purine metabolism in practically all lower animals. This relation has not been established for the human organism, however. Even in the case of man, however, the metabolic relations of allantoin are assuming a new and increasing importance. The researches of Wiechowski, already referred to, aided by his excellent method for the accurate determination of the urinary constituent, have been the most important factors in demonstrating the actual role of allantoin in metabolism.

The allantoin present in the urine originates from two sources. Abundant evidence of *exogenous* allantoin has been furnished in the many feeding experiments to which reference has already been made. The ex-

[1] *Z. physiol. Chem.*, 42, 213 (1904).
[2] *Am. J. Physiol.*, 13, 30 (1905).
[3] *J. Biol. Chem.*, 8, 449 (1910).
[4] *Ibid.*, 7, 171 (1910).
[5] *Z. physiol. Chem.*, 61, 413 (1909).
[6] Eck, *Militär-Medicinischer J.*, 132, 1877. Hahn, Massen, Nencki and Pavlov, *Arch. exp. Path. und Pharm.*, 32, 161 (1893). Sweet, *J. Exp. Med.*, 6, 161 (1905). Hawk, *Am. J. Physiol.*, 21, 259 (1908).

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perimental bases for the claims of an endogenous allantoin excretion are more meagre but none the less convincing. The first experimental evidence so far as we are aware which indicated an endogenous source of allantoin was the report of Underhill and Kleiner,[1] to the effect that they had found that substance in the urine of two fasting dogs. They could, however, demonstrate no uniformity in the daily output of allantoin nor any relation between the allantoin excretion and the purine output. About the same time Wiechowski[2] made an examination of the urine of dogs after short fasts and reported a fairly uniform allantoin output from day to day. Later came the report by Schittenhelm[1] of a similar finding. The percentage of the total nitrogen which was excreted in the form of allantoin, however, decreased during the final days of the fast. The last work upon the allantoin excretion of the fasting organism is that very recently reported by Hunter and Givens[1] in which they show the daily output of a fasting coyote to be very uniform from day to day of an eight-day fast.

Only a portion of the purines of the diet appear in the urine as uric acid. A portion is further oxidized and appears in the form of allantoin. The action of nucleases, deamidizing and oxidizing enzymes, upon the nucleic acids and purine compounds are factors in influencing the output of purine nitrogen in the urine. The problem of uric acid formation, decomposition and retention also has an important bearing. So far as the urinary purine base excretion is concerned, the most extensive investigations have been made by Krüger and Salomon.[3] They isolated the following quantities of purine bases from 10,000 liters of human urine: 1-Methyl-xanthine, 31.32 g.; heteroxanthine, 22.35 g.; paraxanthine, 15.32 g.; xanthine, 10.12 g.; hypoxanthine, 8.51 g.; adenine, 3.54 g.; epiguanine, 3.4 g. The feeding of meat, thymus, spleen, etc., produces an increased output of purine bases in the urine.

The purine excretion of fasting animals has been observed in but few instances. The investigations of Underhill and Kleiner, Schittenhelm and Hunter and Givens[4] are the most important. The first two investigations were made upon dogs, whereas a coyote was the subject of the third experiment. Underhill and Kleiner showed the output of purine nitrogen to be irregular during a thirteen-day fast with no decided tendency toward either a decrease or an increase as the fast progressed. The same in general is true of Schittenhelm's findings. In the work of Hunter and Givens no attempt was made to follow the course of the purine output, the analyses being made on a composit urine sample.

[1] *Loc. cit.*

[2] Hofmeister's *Beitr.*, 11, 109 (1908).

[3] *Z. physiol. Chem.*, 24, 364 (1897); *Ibid.*, 26, 350 (1898).

[4] Underhill and Kleiner, *Loc. cit.* Schittenhelm, *Loc. cit.* Hunter and Givens, *Loc. cit.*

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A very interesting and important relationship has been observed by Schittenhelm and by Hunter and Givens between the allantoin and purine excretions. The first mentioned investigator, for example, after feeding 0.26 gram of purine nitrogen to a fasting dog, recovered 0.25 gram in the urine of the following 24 hours. This was 96 per cent. of the ingested amount. It is very significant that of this 96 per cent., allantoin furnished 95 per cent., purine bases 4 per cent., and uric acid 1 per cent. In the case of the fasting coyote Hunter and Givens found 95.7 per cent. of the nitrogen of purine origin to be excreted in the form of allantoin, whereas but 4.3 per cent. was eliminated as urinary purine nitrogen; when the coyote was fed a meat diet the corresponding percentages were 97.2 and 2.8, respectively.

Plan and Methods.

In the present paper data are given for the allantoin and purine excretions of three fasting dogs and a comparison made between these data and those already reported[1] from a fourth fasting dog. Two of the three dogs under investigation (dogs 2 and 3) were adult males, whereas the third (dog 6) was a male pup one month old. The fasts of the adult dogs were 48 and 96 days in length, respectively, whereas the pup fasted only a week. Previous to the fast the adult animals were fed a diet of meat, cracker meal, lard and bone ash; the pup was given a milk ration. The quantities of the various dietary constituents fed these animals during each day of the preliminary period are listed in Table I. For

TABLE I.—DAILY DIETS.
(Grams.)

	Meat.	Cracker dust.	Lard.	Bone ash.	Water.
Dog No. 2	250	70	30	10	500[2]
Dog No. 3	400	100	45	12	700[2]
Dog No. 6	100 cc. of milk[3]				

chemical analysis of the foods see the paper by Howe and Hawk,[4] already mentioned. The body weights (kg.) of the animals were as follows:

	End of preliminary period.	End of fast.
Dog No. 3	26.33	11.32
Dog No. 2	13.64	6.42
Dog No. 6	1.34	1.05

In each instance approximate nitrogen equilibrium was secured during a preliminary period in which the dogs were caused to ingest a uniform

[1] Howe and Hawk, THIS JOURNAL, 33, 215 (1911).

[2] During each day of the fast the volume of water was fed by means of a stomach tube.

[3] During the fast this animal received 100 cc. water per day by means of a stomach tube.

[4] THIS JOURNAL, 33, 215 (1911).

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diet of constant water content.[1] When a satisfactory nitrogen balance was secured the fast began.

So far as possible, each individual 24-hour urine sample was subjected to analysis. In a few instances, and particularly in the case of dog No. 3, composit samples of urine were analyzed, including aliquot portions from the urinary output of periods ranging from 5 to 10 days in length. The method used for the determination of allantoin and purine nitrogen was that of Paduschka[2] as modified by Underhill and Kleiner.[2] Unfortunately, the superior method of Wiechowski was not reported until we were well along on our experiment. In another investigation now under way in this laboratory Wiechowski's method is being employed.

In Tables II, III and IV will be found the data for the allantoin and purine excretions of dogs Nos. 2, 3, and 6, whereas Table V contains data from the fourth dog already mentioned.

Discussion of Results.

Allantoin Excretion. Allantoin Excretion of Dog No. 3.—The data concerning the allantoin output of this animal will be found in Table II. An examination of this table will show that the average daily output of allantoin nitrogen for the feeding period was 0.051 gram, or 0.22 per cent. of the total nitrogen output for that time. The elimination of nitrogen in the form of allantoin during the course of the 96-day fast was irregular. In general, however, there was a tendency toward a *decreased allantoin excretion* as the fast progressed. This is shown very clearly; for example, if we compare the total output of allantoin-nitrogen for thirty days in the early part of the fast with the output for a similar period at the end of the fast. The actual output of allantoin-nitrogen for thirty days early in the fast was 0.4 gram, whereas the similar value for the latter part of the 96-day fast was 0.24 gram. It is evident, therefore, that this animal excreted only 60 per cent. as much nitrogen per day in the form of allantoin during the advanced stages of fasting as was eliminated during the early stages of the period. As compared with the feeding period, the values for the average daily allantoin-nitrogen excretion are as follows: Feeding period = 0.051 gram; early stage of fasting (4–38 days) = 0.013 gram; late stage of fasting (67–96 days) = 0.008 gram. None of the other investigators mentioned as having investigated the allantoin excretion of fasting animals[3] have reported a pronounced decrease of this nature in the allantoin excretion in the final stages of the fast. This

[1] Fowler and Hawk, *J. Exp. Med.*, 12, 388 (1910). Hawk *et al.*, Proceedings of the Second International Congress of Alimentary Hygiene and the Rational Feeding of Man (Bruxelles, 1910), Vol. I, Section 2, p. 30.

[2] *Loc. cit.*

[3] Schittenhelm, *Loc. cit.* Underhill and Kleiner, *Loc. cit.* Hunter and Givens, *Loc. cit.*

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may be due to the fact that the 96-day fast here considered is much longer than the fasting periods utilized by the investigators in question.

TABLE II.—ALLANTOIN AND PURINE EXCRETION.

Dog. No. 3. Daily averages.

Day of expt.	Allantoin-nitrogen. Total. Gram.	Daily average. Grams.	Per cent. of total nitrogen.	Purine-nitrogen. Total. Gram	Daily average. Grams.	Per cent. of total nitrogen.
		Preliminary Period.				
Av. for period		0.051	0.22		0.067	0.29
		Fasting Period.				
1	...	...	....	0.098	0.098	1.05
2	...	...	....	...	...	....
3	...	...	....	...	...	....
4	0.065	0.065	0.72	0.035	0.035	0.39
5	0.025	0.025	0.53	0.020	0.020	0.42
6	...	...	....	...	...	....
7	0.021	0.021	0.68	0.013	0.013	0.42
8	0.028	0.028	0.53	0.021	0.021	0.40
9	...	...	....	...	...	....
10	0.021	0.021	0.34	0.024	0.024	0.39
11	...	...	....	...	...	....
12	...	...	....	...	...	....
13	0.014	0.014	0.34	0.018	0.018	0.44
14	0.007	0.007	0.42	0.010	0.010	0.60
15	0.100	0.100	0.41	0.006	0.006	0.25
16	0.025	0.025	0.53	0.013	0.013	0.28
17	0.008	0.008	0.23	0.020	0.020	0.58
18	...	...	....	0.023	0.023	0.38
19	0.003	0.003	0.24	0.004	0.004	0.32
20–29	0.019	0.002	0.56	0.139	0.014	0.41
30–38	0.066	0.007	0.24	0.114	0.013	0.42
39–49	0.065	0.006	0.20	0.181	0.016	0.56
50–59	0.111	0.011	0.36	0.153	0.015	0.50
60	0.036	0.036	0.71	0.005	0.005	0.10
61	0.024	0.024	0.65	0.004	0.004	0.11
62	0.036	0.036	1.16	0.002	0.002	0.07
63	0.028	0.028	1.00	0.002	0.002	0.07
64	0.016	0.016	0.71	0.002	0.002	0.09
65	0.018	0.018	0.60	0.012	0.012	0.40
66	0.010	0.010	0.46	0.007	0.007	0.32
67–71	0.030	0.006	0.20	0.131	0.026	0.88
72–76	0.031	0.006	0.18	0.036	0.007	0.21
77–81	0.027	0.005	0.20	0.048	0.010	0.36
82–86	0.040	0.008	0.26	0.037	0.007	0.24
87–91	0.048	0.010	0.37	0.047	0.009	0.36
92–96	0.065	0.013	0.51	0.034	0.007	0.27

When we come to consider the percentage of the total nitrogen excretion of the various fasting days which was eliminated in the form of allantoin we find a decrease during the latter part of the fast, which is fairly

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comparable to the decrease in the actual allantoin elimination for that period. It is significant that this decrease is secured notwithstanding the fact that the actual output of allantoin, as well as the percentage excretion, is seen to undergo a gradual increase from the 72nd to the 96th day. Even this progressive increase, however, does not cause the allantoin values for the 96th day to equal those of the 64th day. In comparison with the percentage values of the feeding period those of the fast are seen to be greatly *increased*. The ingestion of 2100 cc. of water per day during a four-day interval (60–63rd day) was marked by a pronounced *increase* in the output of allantoin. This point receives further consideration in a later paragraph.

TABLE III.—ALLANTOIN AND PURINE EXCRETION.

Dog No. 2.

Day of expt.	Daily output. Output of allantoin-nitrogen. Gram.	Per cent. of total nitrogen.	Output of purine-nitrogen. Gram.	Per cent. of total nitrogen.
		Preliminary Period.		
5–9	0.016	0.19	0.054	0.64
		Fasting Period.		
10	0.025	0.97	0.006	0.23
11	...	....	...	....
12	0.010	0.17	0.039	0.66
13	0.008	0.23	0.011	0.31
14	0.016	0.66	0.005	0.21
15	0.006	0.21	0.004	0.14
16	0.006	0.21	0.003	0.10
17	0.002	0.11	0.003	0.16
18	0.007	0.17	0.007	0.17
19	0.002	0.08	0.005	0.19
20	0.004	0.14	0.003	0.11
21	0.019	0.63	0.007	0.23
22	0.007	0.32	0.008	0.36
23	0.011	0.29	0.012	0.32
24	0.011	0.36	0.020	0.65
25	0.007	0.53	...	....
26	0.017	0.53	0.016	0.50
27	0.020	0.50	0.015	0.37
28	0.020	0.74	0.014	0.52
29	0.003	0.18	0.008	0.48
30	0.019	0.90	0.006	0.28
31	0.019	0.89	0.006	0.28
32	0.020	0.36	0.016	0.29
33	0.016	0.65	0.009	0.36
34	0.021	0.64	0.010	0.31
35	0.016	0.69	0.010	0.43
36	0.019	0.73	0.014	0.54
37	0.019	0.72	0.002	0.08
38	0.024	0.69	0.006	0.17
39	0.015	0.62	0.007	0.29

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TABLE III (*Continued*).

Day of expt.	Output of allantoin-nitrogen.		Output of purine-nitrogen.	
	Gram.	Per cent. of total nitrogen.	Gram.	Per cent. of total nitrogen.
40	0.015	0.62	0.007	0.29
41	0.008	0.34	0.006	0.25
42	0.008	0.34	0.006	0.25
43	0.006	0.22	0.005	0.23
44	0.006	0.22	0.005	0.23
45	0.011	0.48	0.006	0.26
46	0.011	0.48	0.006	0.26
47	0.013	0.43	0.005	0.17
48	0.013	0.43	0.005	0.17
49	0.016	0.55	0.005	0.17
50	0.016	0.55	0.005	0.17
51	0.017	0.61	0.006	0.22
52	0.017	0.61	0.006	0.22
53	0.012	0.36	0.007	0.21
54	0.012	0.36	0.007	0.21
55	0.019	0.46	0.014	0.34
56	0.019	0.44	0.014	0.33
57	0.033	0.55	0.008	0.13

Allantoin Excretion of Dog No. 2.—The data from this animal are tabulated in Table III. An examination of this table will indicate that the average daily output of allantoin-nitrogen during the days of normal feeding preceding the fast was 0.016 gram, or 0.19 per cent. of the total nitrogen excretion for that period. With the inception of the fast this value rose on the first day to 0.025 gram, or 0.97 per cent. of the total nitrogen output. This was the second largest output of allantoin-nitrogen secured during the fast, the largest being an output of 0.033 gram which was eliminated upon the very last day of the experiment. Although the output of 0.025 gram excreted upon the first fasting day was not so large as that secured upon the 48th day of fast, it did, nevertheless, constitute a greater proportion of the total nitrogen than did the 48th day excretion of 0.033 gram. The latter value was only 0.55 per cent. of the total nitrogen eliminated on that day, whereas the allantoin quota for the first day constituted 0.97 per cent. of the total nitrogen output, as already mentioned.

In general, the allantoin-nitrogen elimination was less during the early part of the fasting period than it was at later stages in the fast. For example, the average daily excretion for the first third of the fast (16 days) was 0.009 gram, for the second third 0.017 gram, and for the remainder 0.014. It will be observed that the daily average excretion for the first part of the fast was much lower than that of the preliminary feeding period, whereas the daily average for the remainder of the fast was very close to the feeding level. The grand average excretion per

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day for the entire 48-day fast was 0.013 gram as compared with an output of 0.016 gram for the preliminary period. There was therefore an actual decrease in the output of allantoin as a result of the fast; the proportion of the total nitrogen of the fasting period which was made up by allantoin-nitrogen was, however, markedly increased. This was increased between 200 per cent. and 300 per cent. during the fast above that in force during normal feeding.

TABLE IV.—ALLANTOIN AND PURINE EXCRETION.

Dog No. 6. Daily averages.

Day of expt.	Allantoin-nitrogen. Total. Gram.	Daily average. Gram.	Per cent. of total nitrogen.	Purine-nitrogen. Total. Gram.	Daily average. Gram.	Per cent. of total nitrogen.
		Preliminary Period.				
7–9	0.001	0.0004	0.32	0.002	0.0007	0.65
10–12	0.002	0.0007	0.35	0.003	0.0010	0.52
Period av.		0.0005	0.34		0.0008	0.56
		Fasting Period.				
13–16	0.004	0.0010	0.17	0.007	0.002	0.29
17–19	0.002	0.0007	0.11	0.006	0.002	0.34
Period av.		0.0009	0.145		0.002	0.31

Allantoin Excretion of Dog No. 6.—The data for this dog are given in Table IV. If this table be examined, it will be noted that the average daily excretion from the 7th to 9th day of the preliminary period was 0.0004 gram or 0.32 per cent. of the total nitrogen output. From the 10th to 12th day of this same period the average daily output was 0.0007 gram, or 0.35 per cent. of the total nitrogen. The grand average daily excretion for the whole preliminary period was 0.0005 gram, or 0.34 per cent. of the total nitrogen excreted during this interval.

The fast continued for a period of one week. During the first four days (13–16) the daily output of allantoin-nitrogen was 0.0010 gram, a value double the daily average of the preliminary period. On the three following days, the output fell somewhat but still remained above that for the preliminary period. The average output for these days was 0.0007 gram. Taking into consideration the entire fast of 7 days the grand average daily output of allantoin-nitrogen was 0.0009 gram, a value which was very nearly double that of the preliminary period.

Notwithstanding the fact that the actual quantity of allantoin-nitrogen eliminated per day was much higher during the fasting interval than during the days of normal feeding, it is a significant fact that the proportion of the total nitrogen output which the allantoin represented was less than one-half as great as it had been previous to the opening of the fast. The table shows that the allantoin accounted for 0.34 per cent. of the total nitrogen during the preliminary period, whereas 0.145 per cent. of the total nitrogen was made up by the allantoin during the fasting inter-

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val. This is a much more striking reversal in the course of the allantoin excretion in the change from normal feeding to a fasting régime than was noted in the case of either of the dogs previously considered.

Comparison of Allantoin-nitrogen Data.—A brief comparison of the data from the analysis of the urine of the three dogs, as well as that of the fourth dog previously mentioned, will be of interest. Of the four dogs under consideration three were adults, dog No. 1 being the youngest of the three (1–2 years of age), whereas one dog (No. 6) was a pup only one month old. We may consider then that we have two distinct types of animal so far as age is concerned.

First let us compare the data from the adults. dog No. 3 exhibited a decreased excretion of allantoin under the influence of the fast. However, when we come to examin into the question of the proportion of the total nitrogen elimination, which this allantoin-nitrogen represents, we see that the percentage underwent a pronounced rise during the fasting interval.

In the case of dog. No. 2 we again observe an actual decrease in the average daily output of allantoin-nitrogen as we change from a feeding to a fasting régime. The decrease is, however, much less pronounced than in the case of dog No. 3. In fact, during the latter $^2/_3$ of the fast the daily output is very nearly equivalent to that of the feeding level. When we consider the relation between total nitrogen and that in the form of allantoin we find a condition similar to that in force with dog No. 3. In other words, the allantoin excretion of the fasting days made up a larger quota of the total nitrogen output than it did during the feeding interval. The difference in this respect was much more marked in the case of dog No. 2 than in the case of dog No. 3.

TABLE V.—ALLANTOIN AND PURINE EXCRETION.

Dog No. 1.

		Daily averages.			
		Purine-nitrogen.		Allantoin-nitrogen.	
Period.	Length in days.	Gram.	Per cent. of total nitrogen.	Gram.	Per cent. of total nitrogen.
Preliminary	8	0.012	0.45	0.008	0.31
First fast	15	0.005	0.22	0.005	0.26
Preliminary feeding	4	0.006	0.45	0.009	0.71
Normal feeding	15	0.006	0.35	0.005	0.28
50 per cent. increase in diet	8	0.007	0.27	0.013	0.50
100 per cent. increase in diet	17	0.015	0.40	0.006	0.15
Normal feeding	3	0.008	0.33	0.005	0.20
Second fast	30	0.005	0.38	0.004	0.31

If we examin the data for dog No. 1, as given in Table V, we will observe that the course of the allantoin-nitrogen excretion was very similar to that secured from the analysis of the urine of dogs Nos. 2 and 3, so far as the actual average daily output of this form of nitrogen was concerned.

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For example, it will be noted that the average daily output of allantoin-nitrogen for the first fast (15 days) to which this animal was subjected was considerably lower than the excretion of the preliminary period calculated upon the same basis. The ratio in this instance is 5 : 8. Again taking the second fast, we here find that in this instance the fasting level of the allantoin-nitrogen elimination is somewhat lower than the feeding plane. The ratio is less pronounced than that in force during the first fast, however, being 4 : 5.

If we consider the percentage of the total nitrogen output of dog No. 1, which was eliminated in the form of allantoin-nitrogen, we find a condition of affairs entirely different from that which was obtained with dogs Nos. 2 and 3. In the first fast of dog No. 1, for example, the allantoin-nitrogen constituted 0.26 per cent. of the total nitrogen whereas this form of nitrogen composed 0.31 per cent. of the total nitrogen excreted during the period of normal feeding. Dogs Nos. 2 and 3, it will be remembered, each exhibited during the fast a very pronounced increase above the feeding value in the percentage of the total nitrogen which appeared as allantoin-nitrogen. The data from dog No. 1, however, show a decreased percentage excretion of allantoin-nitrogen as we pass from feeding to fasting. In other words, the course of the percentage allantoin output for this animal during the first fast exhibits the characteristics of the percentage allantoin output of the pup (dog No. 6). The decrease in the percentage values, however, was much sharper in the case of the pup. When we turn to the second fast of dog No. 1 we find that the conditions regarding the percentage elimination of allantoin-nitrogen are reversed and are rather more in keeping with those from the adult dogs Nos. 2 and 3. The increase in the percentage values during this second fast is still much less, however, than that previously observed in the case of these two animals.

It seems, therefore, when we take into account the allantoin values from the four dogs in question that there are pronounced variations in the actual output of allantoin as well as in the ratio which this output bears to the total quantity of nitrogen excreted per day. With dog No. 3 the change in the course of the allantoin excretion as we passed from feeding to fasting consisted in a pronounced *decrease in the quantity of allantoin actually excreted*, accompanied by a much more pronounced *increase in the percentage relationship* between this allantoin output and that of total nitrogen. With dog No. 2, while there was a decrease in the actual quantity of allantoin excreted per day, this decrease was small as compared with that observed in connection with dog No. 3. The increase in the percentage values was rather more decided, however, in this fasting animal than in No. 3. In opposition to these findings, we observe when we turn to the pup that the fasting period yields us an *increase in*

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the actual quantity of allantoin-nitrogen excreted per day and at the same time furnishes a *decrease in the percentage of the total nitrogen* which this allantoin-nitrogen represents. Here, then, we have a decided contrast in the course of the allantoin excretion of the adult dogs as compared with that of the animal but lately weaned. The course of the allantoin excretion of dog No. 1 apparently stands midway between those of the adult animals 2 and 3 and the pup (6). We have a decrease in the output of allantoin-nitrogen during the fast as compared with the feeding level, a feature which is held in common by adult dogs Nos. 2 and 3. The decrease is, however, much less pronounced than that observed in the data for 3. The percentage of the total nitrogen which is excreted as allantoin undergoes a *decrease* as a result of the first fast, a finding in accord with the data from the pup and directly opposit to the percentage values for the allantoin excretion of the adult dogs. As we pass from normal feeding to the second fast an *increase* in the percentage values is observed, but this increase is in no way comparable to the more marked increase which was in force during the fasts of dogs Nos. 2 and 3. It is an interesting and very significant finding that this animal, which stood in an intermediate position between the adult dogs and the pup as regards age, should yield allantion values which also occupy an intermediate position between the allantoin values furnished by the other dogs in question.

Purine Excretion. Purine Excretion of Dog No. 3.—The data from the purine excretion of this animal are given in Table II. It will be observed that the average daily output of purine-nitrogen during the preliminary period was 0.067 gram, or 0.29 per cent. of the total nitrogen excreted. On the first day of the fast the actual amount of this form of nitrogen which was eliminated in the urine rose to 0.098 gram, a value which constituted 1.05 per cent. of the total nitrogen excreted during that 24-hour interval. At no time in the remaining 95 days of the fast did these values approach those secured upon the first day. This very marked increase in the purine excretion upon the first fasting day is a very significant finding.

There was no very decided regularity in the average daily output of purine nitrogen during the fast, although the average was decidedly lower during the second half of the fast than it was during the first half. The average percentage values were also lower during the later stages of the fast than they were during the earlier stages, although the variation in this respect was not very marked. Under the influence of a pronounced increase in the water ingestion, the purine-nitrogen excretion underwent a profound *decrease* from the 60th to the 63rd day, inclusive. This feature is further discussed in a later paragraph.

Purine Excretion of Dog No. 2.—For data regarding this subject see Table III. These data indicate that the average daily output of purine-

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nitrogen during the period of normal feeding was 0.054 gram or 0.64 per cent. of the total nitrogen value. On the first day of the fasting period these values were subjected to a profound alteration. It will be noted that the actual quantity of purine-nitrogen excreted on this day amounted to but 0.006 gram, a weight which was equivalent to only 0.23 per cent. of the total nitrogen output for that 24-hour interval. This pronounced lowering of these values upon the first fasting day is in marked contrast with the first-day findings for the other adult dog (3). With this dog (3), as already mentioned, the actual quantity of purine-nitrogen eliminated upon this day as well as its percentage relationship to the total nitrogen excretion both underwent a very *decisive increase*, whereas in the case of dog No. 2 the result was a *decrease* which was fully as marked as the increase had been in the case of dog No. 3.

The maximum fasting excretion (0.039 gram) for dog No. 2 occurred on the 3rd day of the fast. This value also made up a larger quota (0.66 per cent.) of the total nitrogen than did the output for any other day of the fast. The average daily output of purine-nitrogen for the first part of the fast was rather higher than that for the second part. This was true in spite of the fact that the last three days of the fasting interval yielded a higher average daily output than was secured for a period of nearly four weeks previously. If we divide the fast into three 16-day periods we find that the average daily output of purine-nitrogen was uniform during the first $^2/_3$ of the fast and underwent a decided decrease in the final interval. The ratio existing between these three intervals is 10 : 10 : 7. In other words, the average output of purine-nitrogen was uniform for a fasting interval of 32 days, at which time it underwent a drop of 30 per cent.

Purine Excretion of Dog No. 6.—In Table IV will be found the purine-nitrogen data from this animal. It will be observed that the average daily output of this form of nitrogen was 0.0007 gram, or 0.65 per cent. of the total nitrogen during the 7th, 8th, and 9th days and that this value was increased to 0.0010 gram, or 0.52 per cent. of the total nitrogen during the 10th, 11th, and 12th days. The grand average daily elimination of purine-nitrogen for this period of normal feeding was therefore 0.0008 gram, or 0.56 per cent. of the total nitrogen.

When the fast opened the daily average fell to 0.002 gram and maintained that level uniformly throughout the entire fast. The percentage of the total nitrogen which was excreted in the form of purine-nitrogen was also very uniform, ranging from 0.29 per cent. to 0.34 per cent. with a grand average of 0.31 per cent.

Comparison of Purine-nitrogen Data.—In the comparison of the allantoin-nitrogen data given in a previous paragraph, it was pointed out that there were very marked differences in the course of this excretion

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observable in connection with the different animals. These variations seemed, to a certain degree, to be functions of the age of the animal. For example, the course of the allantoin-nitrogen excretion of the month-old pup was widely divergent from that of the adult dogs and furthermore the dog (No. 1) which occupied an intermediate position between the adults on the one hand and the pup on the other, so far as age was concerned, exhibited this same intermediate relationship in respect to allantoin excretion.

When we come to consider the purine-nitrogen data from the comparative view point we find no such relationship as that noted for allantoin. It will be observed, for example, that adult dog No. 2, in passing from the feeding period to the fast, exhibited a *decrease* in both the actual quantity of purine-nitrogen excreted per day and in the percentage of the total nitrogen output which this represented. If we now compare these findings with the data from the pup we find a *similar relationship, i. e.*, a decrease in both the actual output and the percentage value. The data from dog No. 1 show a similar relationship during her first fast, whereas the percentage values were slightly increased during the second fast. When we turn to the data on the purine-nitrogen output of dog No. 3 we find for the first time an important variation from the uniform relations which the purine data have thus far shown. Here we note the same decrease in the actual quantity of purine-nitrogen eliminated per day, but a consideration of the percentage data reveals for the first time an increase in the percentage of the total nitrogen output, which this form of nitrogen comprizes. This increase is approximately 30 per cent. above the value for the preliminary period. It is worthy of note that this increase would have been greater had the purine-nitrogen output not been subjected to a marked diminution during the 60–63rd days, through the influence of a high water intake. This feature of the investigation is discussed in full in the next section.

Influence of a Pronounced Increase in the Water Ingestion of a Fasting Animal upon the Allantoin and Purine Output.—It will be observed upon examining Table II that the daily output of allantoin as well as the percentage of the total nitrogen which is excreted in this form both undergo a sharp rise during the period represented between the 60th and 63rd days, inclusive. This rise in the allantoin output is not due to fasting. Up to this time the dog had been receiving 700 cc. of water per day by means of a stomach tube and during the period in question (60–63rd days), this water ration was increased 200 per cent. It was evidently due to the introduction of this extra volume of water that the heightened allantoin output appeared. Previous to the high water intake the animal had been excreting on an average 0.011 gram of allantoin-nitrogen per day, or 0.36 per cent. of the total nitrogen output. The influence of this

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2100 cc. of water was observed at once, inasmuch as an allantoin-nitrogen output of 0.036 gram, or 0.71 per cent. of the total nitrogen excretion, was secured upon the first day of its ingestion. The allantoin output increased still further and upon the third and fourth days of this copious water ingestion it was equivalent to 1.16 per cent. and 1.00 per cent. of the total amount of nitrogen eliminated. The high values for the allantoin output disappeared as soon as the original level of water ingestion was again assumed.

How is this marked increase in allantoin output during the period of copious water intake to be explained? If we examin the purine data for this same period we will note that there was a pronounced diminution in the output of purine-nitrogen during the days upon which the allantoin-nitrogen was undergoing the striking increase already mentioned. For forty days previous to the period of high water ingestion the dog had been eliminating from 0.013 to 0.016 gram, or 0.41 to 0.56 per cent. of the total nitrogen in the form of purine-nitrogen. At the opening of the water period these values dropped to 0.005 gram, or 0.10 per cent., at which point the purine output remained uniform for two days, then underwent a further decrease to 0.002 gram, or 0.07 per cent., a level which was maintained for the remainder of the water period. There was therefore a very marked *decrease* in the output of purine-nitrogen during the water period, and coincidently with this lowered output of purine-nitrogen comes the pronounced *increase* in the allantoin-nitrogen excretion. In the light of our present knowledge as to the metabolic relationship of purines and allantoin there is apparently but one interpretation to be placed upon these findings. It has been shown by experimentation that purine bodies may be oxidized with the resultant formation of allantoin. It has furthermore been demonstrated that the allantoin output may be increased by purine feeding. It seems clear then that in the present instance the increase in the allantoin excretion and the associated decrease in the purine output are due to the fact that the large volume of water (2100 cc.) fed the dog on each of the days of the water period has stimulated the oxidative processes of the organism to a profound degree. Through the medium of this increased oxidation such substances as would ordinarily be eliminated in the urine and go to increase the purine-nitrogen output have been oxidized to allantoin and appear in the urine in this form. An examination of the data will show that the oxidation of the nitrogen of purine origin into allantoin was almost quantitative in the final days of the water period. For example, on the 62nd day of the experiment the total elimination of nitrogen of purine origin was 1.23 per cent., of which all but 0.07 per cent. was in the form of allantoin. Again, on the 63rd day, with a total output of 1.07 per cent. of nitrogen of purine origin, all but 0.07 per cent. of this nitrogen was

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excreted as allantoin. The purine-nitrogen output was still low for one day immediately after the water period, but from this point on to the end of the experiment the figures for this type of nitrogen were more nearly comparable to those secured during the period previous to the interval of high water ingestion.

The allantoin and purine data of the water period are of further interest in connection with the output of uric acid under the influence of copious water drinking. In another paper from this laboratory[1] it was shown that in man a *decreased* output of uric acid accompanied copious water drinking. Inasmuch as the Folin method for the determination of this urinary constituent had been shown to be rather inaccurate when used to determin the uric acid content of very dilute urines no particular significance was attached to the data which indicated a lowered uric acid output under the influence of water drinking. However, if we take our allantoin and purine findings into account in this connection, we have a very plausible explanation for the phenomenon of a lowered uric acid excretion under such conditions. Evidently when water in large quantity is ingested the nuclein material which gives rise to the uric acid of the urine is subjected to a more profound oxidation than under the régime of a low water ration. Through the medium of this augmented oxidation a certain quota of the uric acid is oxidized and may appear in the urine as allantoin. If this is true, then we would obtain a lowered output of uric acid under the influence of copious water drinking. In the work already referred to as having been done in this laboratory it may very well be that the inaccuracy in method may not be entirely responsible for the low uric acid values obtained during the days of high water ingestion. There may have been an *actual decrease* in the quantity of uric acid eliminated upon those days, due to its oxidation into allantoin. The contention of Schöndorf[2] and of Genth,[3] who claim to have demonstrated a lowered output of uric acid after water drinking, may be worthy of consideration, although their methods were rather open to criticism. On the other hand, if water does cause this increased oxidation of uric acid into allantoin it is hard to reconcile the findings of Laquer[4] and of Schreiber,[5] each of whom maintains that the uric acid output is slightly *increased* under the influence of an increased water ration. Of interest in this connection are the findings of Beebe[6] in his study of the influence of alcohol upon the uric acid output. The ingestion of 50 cc. of absolute alcohol (diluted to 200 cc. with water) by a man caused the hourly urine

[1] Rulon and Hawk, THIS JOURNAL, 32, 1686 (1910).
[2] *Arch. ges. Physiol.*, 46, 529.
[3] Quoted by Schöndorf, *Arch. ges. Physiol.*, 46, 529.
[4] Kongress für innere Medicin, 1896, p. 381.
[5] Schreiber, "Die Harnsaüre," 1899, p. 38.
[6] *Am. J. Physiol.*, 12, 120 (1904).

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volume to increase from 110 cc. to 465 cc. and then to 565 cc., the volume thereafter dropping abruptly to 57 cc. and 35 cc. during the next two one-hour intervals. Accompanying this diuresis a *pronounced decrease* in the output of uric acid was noted. The author says "Sweeping urates out of the system by increasing the volume of water excreted finds little support in this experiment." Mendel and Brown[1] also failed to find any correlation between an increased urine flow and an augmented uric acid output.

It is a significant fact that the total output of nitrogen of purine origin,[2] *i. e.*, purine-nitrogen plus allantoin-nitrogen, was *increased* during the period of high water intake. For forty days previous to the commencement of the water period the total daily output of nitrogen of purine origin had ranged from 0.007 to 0.026 gram, the average for the forty days being 0.021 gram. With the opening of the water period the average of 0.021 gram was increased to 0.041 gram, whereas values of 0.028 gram, 0.038 gram and 0.030 gram were obtained for the remaining days of the period, all of them being considerably above the pre-water average. The daily average for the water period was 0.034 gram as against an average of 0.021 gram for the forty days immediately preceding this period, and 0.019 gram for the 33 days following the period. It is thus evident that there was a definit increase in the total quantity of nitrogen of purine origin which was excreted per day during the period of high water intake. We would interpret this finding as indicating that the water caused a stimulation of the catabolism of muscular tissue and a consequent increase in the output of total purine (allantoin + purine).

The total nitrogen data from this animal show that there was an average daily elimination of 2.872 grams of nitrogen for 6 days previous to the water period, an output which was augmented to an average excretion of 3.669 grams under the influence of water. There was therefore an actual increase of 3.188 grams of nitrogen during the four-day period in which the animal received 2100 cc. of water per day. If we express this nitrogen value in terms of flesh we find it is equivalent to 98 grams, and if we go still further and calculate the amount of purine nitrogen which this weight of flesh should yield if catabolized, we learn that this is 0.059 gram of pure nitrogen. We can readily determin from an examination of the tabulated data that the actual increase in the output of total purine-nitrogen as determined during the water period was 0.032

[1] *J. Am. Med. Assoc.*, 49, 896 (1907).

[2] Professor F. G. Benedict tells us he recalls having read some years ago an article on water drinking which recorded an increased output of nitrogen of purine origin. However, neither Professor Benedict nor ourselves have been able to locate the reference.

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gram. In other words, if 98 grams of flesh were catabolized we cannot account for 46 per cent. of its contained purine-nitrogen. This portion of the purine-nitrogen may have been oxidized to stages below allantoin and thus escaped detection. The calculations mentioned above are summarized below:

RELATION BETWEEN TOTAL NITROGEN AND TOTAL PURINE NITROGEN (ALLANTOIN + PURINE) EXCRETIONS UNDER INFLUENCE OF WATER.

Average daily elimination of total nitrogen[1] for 6 days previous to water period	2.872	grams
Average daily elimination for water period	3.669	"
Daily increase in total nitrogen output during water period	0.797	"
Total increase in total nitrogen output during water period	3.188	"
Equivalent in terms of flesh (3.25 per cent.)	98.0	"
Percentage of purine-nitrogen in flesh	0.060	per cent.[2]
Average daily ouput of total purine-nitrogen for 10 days preceding water period	0.026	gram
Average daily output during water period	0.034	"
Total increase during the 4-day water period	0.032	"
Purine-nitrogen in 98 grams of flesh	0.059	"
Purine-nitrogen unaccounted for	0.027	" or
	46.0	per cent.

The two theories which have been advanced by different investigators to account for the increased nitrogen output which accompanies water drinking have been fully discussed in previous papers from this laboratory.[3] In the paper by Fowler and Hawk were presented data which appeared to furnish, for the first time, conclusive evidence in substantiation of the theory that this increased nitrogen output was due, at least in part, to the catabolism of muscular tissue. The appearance of creatine in the urine during the water period was believed to furnish this evidence. We now submit our total purine data as further substantiation for this same theory. As far as we can see, the total purine nitrogen output of this fasting dog could have been increased during the water period only through the influence of the water in stimulating protein catabolism. To be sure when we come to correlate the total nitrogen data with the total purine nitrogen data we can account for only about one-half of the total nitrogen output on the basis of our purine figures. However, we could logically hardly expect a quantitative result here when we take into account the character of the method and the further fact that the allantoin output may very well have been lowered through the subsequent oxidation of a certain portion of this substance into other undetermined nitrogenous substances.

[1] These data will be published in a forthcoming article.

[2] Hall, "The Purine Bodies in Foodstuffs," Manchester, 1902, p. 29, Table IV.

[3] Hawk, Univ. of Penn., *Medical Bulletin* 18, 7 (1905). Fowler and Hawk, *J. Exp. Med.*, 12, 388 (1910). Wills and Hawk, unpublished.

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In any attempt to show a mathematical relationship between the urinary total purine nitrogen and the total nitrogen output as given in an earlier paragraph, it must be borne in mind that the flesh of the different portions of the same animal will vary in their purine values. For example, Hall[1] has shown that pork loin may contain 0.048 per cent. of purine-nitrogen, whereas the neck may contain but 0.023 per cent. At the same time the neck cut of a calf may contain 0.030 per cent. while the loin contains 0.071 per cent.[2] The purine values of ox flesh have been placed at 0.062 per cent. and 0.063 per cent., whereas horse flesh has been found to yield 0.055 per cent. of purine-nitrogen.[3] It is without doubt true that any factor which stimulates protein catabolism through the medium of the circulation, as does water, must of necessity stimulate this process in all parts of the organism, the stimulatory influence being greatest in those portions which have the most plentiful blood supply. In the case in point, therefore, with our fasting dog, the increased output of total purine nitrogen has no doubt resulted from the stimulated catabolism of tissues which have ranged in purine values from 0.030 to 0.063 per cent. at least. There is obviously no possible way of estimating what percentage of this increased output is due to the disintegration of the one type of tissue as distinct from the others. If we were to make our calculations on the basis of the 0.030 per cent. value, it would be possible to show an almost quantitative relationship between the excretion of total purine-nitrogen and total nitrogen. Such a calculation could, however, have but slight significance. We have therefore taken 0.060 as the basis of our calculations, for the reasons that the portions of the animal which yield such low purine values as 0.030 form in all cases but a minimum portion of the total weight of the carcass. This value of 0.060 per cent. is also suggested by Burian and Hall[1] as a satisfactory average for the purine-nitrogen value of flesh.

Summary.

The experiments here reported embraced the study of the course of the allantoin-nitrogen and purine-nitrogen excretion of four dogs which were subjected to fasting periods ranging in length from one week to 96 days. Water was fed by means of a stomach tube in uniform quantity from day to day during the fast, the volume being regulated according to the body weight of the animal. The adult dogs fasted from 48 to 96 days, whereas a pup one month of age was the subject of the 7-day fast.

When the data for the allantoin-nitrogen excretion of the various dogs are compared, pronounced variations are noted between the different dogs and these variations appear to be functions of the age and develop-

[1] *Loc. cit.*

[2] Burian and Hall, *Z. physiol. Chem.*, 38, 336 (1903).

[3] Burian and Hall, *Loc. cit.*

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ment of the animals in question. For example, in the case of the adult animals we have a *decreased* output of allantoin-nitrogen when the feeding period gives way to a fasting régime, whereas in the case of the pup the allantoin values are nearly *double during the fasting interval* over those secured during the period of normal feeding. Likewise, when we turn to a consideration of the percentage relationship we find that the percentage of the total nitrogen which is excreted as allantoin is *increased* in the case of the adult dogs and *decreased* in the case of the pup. When the data secured from the adult dogs and the pup are compared with those secured from a dog midway between these two types of animal, so far as age is concerned, we find that the course of the allantoin-nitrogen values was also of an intermediate character.

The output of purine-nitrogen does not show the variation noted in connection with the allantoin-nitrogen. There was a well defined tendency toward a *decreased excretion* of purine-nitrogen as well as a *decreased percentage relationship* as the well-nourished animals were subjected to the withdrawal of food. In other words, during the fast there was, in general, a lower elimination of allantoin-nitrogen than during the feeding period and this lowered elimination also constituted a smaller percentage of the total nitrogen output. This percentage relationship did not hold for one dog which fasted 96 days and exhibited an increased percentage relationship during the fast above that in force during the period of normal feeding.

The question of the influence of a *pronounced increase in the water ingestion of a fasting animal* upon the allantoin and purine excretion was studied upon one adult dog. This dog received 700 cc. of water daily for 59 fasting days and for a period of four days from this time the water ingestion was increased to 2100 cc. per day. This high water ingestion produced a *marked increase in the output of allantoin-nitrogen* and a much more *pronounced decrease in the purine-nitrogen* output. These findings were interpreted as indicating that the high water ingestion had caused sufficient stimulation of the oxidative processes of the body to bring about the oxidation into allantoin of such substances as would ordinarily go to make up the purine-nitrogen quota. This oxidation was almost quantitative during the latter part of the water period. During this interval only 0.07 per cent. of the nitrogen of purine origin was excreted in the form of purine-nitrogen. The finding of a lowered output of purine nitrogen was in full agreement with the finding already reported from this laboratory of a lowered output of uric acid under the influence of copious water drinking.

It was further found that the *total purine* values (sum of the allantoin-nitrogen and purine-nitrogen) for the four days of increased water ingestion were higher than the total purine values for any other four-day

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period during the fast. This finding was interpreted as indicating that the high water intake had caused a stimulation of protein catabolism. The total nitrogen was also increased. Knowing the percentage of purine-nitrogen in flesh and the percentage of total nitrogen in flesh a relationship was established between the output of purine nitrogen and the total nitrogen excretion. By this means it was learned that, provided sufficient flesh was catabolized to yield the increased output of total nitrogen eliminated during the water period, 46 per cent. of the purine-nitrogen of this quantity of flesh was unaccounted for. This quota of purine-nitrogen might have been oxidized to stages below allantoin and thus escaped determination.

We submit the data showing an increased output of total purine-nitrogen (allantoin-nitrogen + purine-nitrogen) under the influence of a high water ingestion as evidence in favor of the hypothesis that the water stimulated protein catabolism.

URBANA, ILL.

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY OF HARVARD MEDICAL SCHOOL.]

THE DETERMINATION OF BENZOIC ACID.

BY OTTO FOLIN AND FRED F. FLANDERS.

Received August 4, 1911.

A recent investigation on cranberries undertaken in this laboratory involved a great many determinations of benzoic acid. Although methods for benzoic acid have undergone much improvement recently, it was soon evident that a great deal of time would be consumed in carrying out the large number of determinations which the work demanded.

The method first used was the second modification of the LaWall and Bradshaw method, described in Bulletin 132 of the Bureau of Chemistry.[1] Considerable experience had previously been had by one of us[2] with this method, and its weak points were well known. The filtration of the alkaline solution is usually very tedious and often nearly impossible. The extraction of the acidified filtrate is slow and difficult, as the tendency to form an emulsion is very great. After the extraction the chloroform must be allowed to evaporate and the residue dried in a desiccator to remove acetic acid, which requires much time. Finally the titration in alcoholic solution with phenolphthalein as indicator is open to criticism. This latter objection has been in some degree overcome by Clark[3] by adding water and titrating directly in the chloroform with aqueous alkali.

It occurred to us that this titration might be better made in the chloroform directly, according to the principle recently advanced by Folin and

[1] U. S. Dept. Agr., Bur. of Chem., *Bull.* 132, p. 140 (method 2).

[2] Flanders.

[3] U. S. Dept. Agr., Bur. of Chem., *Bull.* 132, p. 147.

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Wentworth.[1] It would only be necessary to make the extraction with chloroform, remove all acids except benzoic from the extract and titrate at once with sodium alcoholate solution.[2] In the work on cranberries, this proved a rather simple matter and the results were satisfactory.

In order to make the method of more general use, its application to the determination of benzoic acid in catchup was attempted. Here the problem was more difficult. A number of acids are extracted from catchup by chloroform. This has already been noticed by Poppe, Jackson[3] and others in connection with the high results generally obtained, but has been attributed in most cases to mineral acids carried through by the emulsion. A very few experiments by our method indicated that oxalic, malic, tartaric, citric, and aminoacetic acids were not extracted from acid salt solution by chloroform, but that acetic, lactic, glycolic, and cinnamic acids were extracted in varying amounts. Acetic and lactic acids, being normal constituents of catchup, would certainly interfere, so that the problem was to free the chloroform from these and possibly other acids without loss of benzoic acid, so that it would be fit for titration without the necessity of evaporating and drying the residue. It was found that a saturated solution of sodium chloride containing a small amount of hydrochloric acid would remove the acetic acid and still not remove appreciable quantities of benzoic acid. When the principle was applied to catchup it was found that some acid or acids were present which were not so readily removed as acetic acid, and that more washings would be required than would be needed to remove acetic acid alone. Even with two washings, using 200 cc. of salt solution for each, the results were always too high by a nearly constant amount. This and other facts indicate that a higher fatty acid is present in catchup in small amount. Numerous tests on different catchups, by our method, show that the amount of this acid is equivalent to about 0.017 per cent. calculated as benzoic acid. Blank tests by the regular method yielded on Snider's catchup 0.017 per cent. and on Heinz's catchup 0.012 per cent. acid calculated as benzoic, when none had been added. Obviously the cause of the high results is to be sought in this non-volatil acid.

In order to simplify the process, the attempt was made to extract the catchup, without filtering. At first the tendency to emulsify made extraction impossible; also much coloring matter and fatty constituents were extracted. Then it was discovered that a small amount of concentrated nitric acid would lessen the trouble with emulsion. Later by adding sodium nitrite, the extractions were made without difficulty, and the coloring matter was almost completely destroyed so that the

[1] *J. Biol. Chem.*, 7, 423.
[2] Previous citation.
[3] U. S. Dept. Agr., Bur. of Chem., *Bull.* 132, p. 142.

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chloroform extract was nearly colorless. Also the amount of fatty material extracted was apparently much diminished. We have also been able to overcome the tendency to emulsify by boiling gently for $1^1/_2$ hours with dilute acid under an air tube condenser, filtering, and extracting the filtrate, after saturating with salt. This was not found practicable with catchups which contained more than 0.1 per cent. of benzoic acid as some of the acid separates out and is lost in filtering. It has given good results, however, in the case of jellies and products which do not need filtering, but in such cases the heating should be brief, only 10 or 15 minutes, else much caramel is formed, which discolors the chloroform.

After numerous experiments the following procedure was adopted:

Twenty-five grams of catchup are weighed out in a 50 cc. beaker, 2 cc. concentrated nitric acid added and the mixture well stirred. Several small portions, about 0.2–0.3 gram in all, of sodium nitrite are added, stirring well after each addition. Without filtering, the bleached mass is rinsed into a 500 cc. separatory funnel by means of 200 cc. of saturated ammonium sulfate solution. Five extractions are made with chloroform using 50, 35, 25, 25, and 25 cc. respectively. The shaking is done by a gentle rotatory motion and the separatory funnel is not to be shaken violently. The separate portions are drawn down as closely as possible, into a second separatory funnel and shaken with 200 cc. of a saturated solution of chemically pure sodium chloride, to each liter of which has been added 3 cc. of 10 per cent. hydrochloric acid. After clearing, the chloroform is drawn into a third separatory funnel and again shaken with a fresh 200 cc. portion of the acidified salt solution.

It is then drawn into a 500 cc. Erlenmeyer flask, 4 or 5 drops of alcoholic phenolphthalein added and titrated with standard sodium alcoholate solution. The first persistent pink color is taken as the end point, although the color may fade on standing. With some samples the chloroform has a light straw color, which may deepen slightly as the titration nears the end, but this causes no difficulty, the end-point being generally sharp and definit.

The standard sodium alcoholate is prepared by dissolving 2.3 grams of cleaned metallic sodium in one liter of absolute alcohol.[1] It is best standardized against pure benzoic acid in the same volume of chloroform as used for the titration, namely 165 cc. It must here be noted that some samples of chloroform develop hydrochloric acid on standing and, particularly when used for standardization, should be shaken with distilled water or dilute sodium hydroxide just before use.

The sodium alcoholate may also be standardized against sodium benzoate by extracting a weighed portion from a saturated salt solution made

[1] *J. Biol. Chem.*, 7, 423.

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distinctly acid with hydrochloric acid, passing the chloroform through a small filter and titrating as before.

It has been stated that the sodium alcoholate may be standardized against aqueous acid.[1] Our recent experience does not quite bear out this statement. The standard in aqueous solution appears to be slightly too high. Numerous experiments indicate that the results on catchup are too high by an amount equivalent to about 0.35 cc. of 0.1 *N* sodium alcoholate when the weight of sample taken is 25 grams.

A number of titrations of known amounts of sodium benzoate are given. If this amount, 0.35 cc., is deducted, the results are in fair agreement with the amounts added.

Sodium benzoate added. Per cent.	Titration. Cc.	Found by deducting 0.35 cc. Per cent.	Brand of catchup.
0.064	1.55	0.0696	Snider's
0.160	3.1	0.1595	"
0.320	5.7	0.3103	"
0.064	1.6	0.0725	Heinz's
0.160	3.1	0.1595	"
0.320	5.85	0.319	"

That at least two acids besides acetic are extracted by the chloroform is shown by the following experiment: An amount of sodium benzoate solution equivalent to 1.1 cc. of the sodium alcoholate was added to 25 grams of catchup and the extraction made as directed. The chloroform was then shaken with successive 100 cc. portions of the acidified salt solution, titrating after each shaking. One acid appears to be removed by the first few treatments with the salt solution, but the other remains constant. It appears also that no benzoic acid is lost by the treatment for the titration remained constant, even after several additional shakings.

	Titration.	Theory.
2nd shaking.....	2.4 cc. sodium alcoholate	1.1 cc.
3rd shaking.....	1.7 cc. "	"
4th shaking.....	1.5 cc. "	"
5th shaking.....	1.4 cc. "	"
6th shaking.....	1.4 cc. "	"
7th shaking.....	1.4 cc. "	"

As before stated, glycolic, lactic, acetic and cinnamic acids were found to interfere. This acid which remains with the benzoic might be cinnamic, but could not be one of the three first mentioned as they are all readily removed by washing with the salt solution. Cinnamic acid acts exactly like benzoic acid and will, when present, be estimated with it.

The apparent advantages of the method are the short time required for analysis, usually only $1^1/_2$ hours, ease of manipulation, time and

[1] *J. Biol. Chem.*, 7, 424.

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trouble of filtering and aliquoting saved, and recovery of the chloroform. Also, the method of titration is itself capable of great exactness. The method would appear to be well adapted to the needs of the manufacturer, for after the extent of the blank had been well established on a given stock, the results should be quite satisfactory.

As a qualitative test, the method is both quick and reliable. It is only necessary to shake the chloroform, after titration, with a small amount of water, separate and filter the aqueous solution to remove emulsion, and test with ferric chloride or apply Mohler's test. The used chloroform may be recovered by shaking several times with water made alkaline with sodium or potassium hydroxide. It should be tested by shaking 100 cc. with dilute hydrochloric acid, separating and titrating with the 0.1 *N* sodium alcoholate. Not more than 0.02 cc. should be required to give the end point with phenolphthalein.

THE CRYSTALLIN ALKALOID OF CALYCANTHUS GLAUCUS.

[FOURTH PAPER.]

SOME SALTS OF A NEW QUATERNARY BASE OBTAINED BY METHYLATING ISOCALYCANTHINE.

By H. M. Gordin.

Received August 1, 1911.

It was shown in the last paper on this subject[1] that anhydrous isocalycanthine has the formula $C_{11}H_{14}N_2$, and that when recrystallized from a mixture of acetone and water, it contains some water of crystallization, the exact amount of which is difficult to determin, owing to the extreme slowness with which this water is given off. When the alkaloid is kept *in vacuo* over a drying agent, the loss of the water of crystallization is at first fast, but very soon slackens down to such an extent that it can be observed only when working upon considerable quantities and weighing every few weeks. I have been keeping 1.9862 grams of the alkaloid in a vacuum desiccator over sulfuric acid for nearly twenty months. So far the loss amounts to 0.0894 gram, and the weight has not changed within the last two months. Supposing there will be no further loss, the amount of water of crystallization found would be 4.5 per cent., corresponding to half a molecule of water. Calculated for $C_{11}H_{14}N_2 \cdot {}^1/_2H_2O$, 4.92 per cent. H_2O.

It was also shown in that paper that the alkaloid contains an NH group, since when treated with nitrous acid, it gives an insoluble nitrosoamine. It was therefore expected that it would react with one molecule of methyl iodide to form a tertiary methyl isocalycanthine of the formula $C_{11}H_{13}(CH_3)N_2$, and with two molecules of methyl iodide to form a neutral

[1] This Journal, 31, 1305.

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quaternary iodide having the formula $C_{11}H_{13}(CH_3)N_2.CH_3I$. A large number of experiments showed, however, that whether the methyl iodide is in excess or the alkaloid is in excess, whether the reaction takes place at ordinary temperature or at 100° under pressure, in no case is either of the expected substances formed. Under all conditions so far tried the products of the reaction are as follows: About 35 per cent. of the isocalycanthine taken takes no part in the reaction, and can be recovered unchanged; about 35 per cent. of the isocalycanthine is converted into its hydriodide, while the rest is transformed into a new quaternary iodide having the entirely unexpected formula $C_{24}H_{28}N_3IO.H_2O$. The relative quantities of these substances were determined by the following procedure: The whole of the reaction product, obtained by evaporating the methyl alcohol and the excess of methyl iodide to dryness, as described below, was taken up with dilute acetic acid (about 6 per cent.). The acid easily dissolves the unchanged isocalycanthine, but takes up only a small amount of its hydriodide produced in the reaction, and still less of the new quaternary iodide, which is very difficultly soluble in water even in presence of weak acids. From the acid solution the unchanged isocalycanthine is obtained by precipitation with ammonia. From 10 grams isocalycanthine taken, 3.5 grams were recovered unchanged. The residue left after treatment with the acetic acid was rubbed up with concentrated ammonia, which liberates the isocalycanthine from its hydriodide formed in the reaction, but does not affect the new quaternary compound, except to make it less soluble in water. After standing over night, the ammoniacal liquid was sucked off, the residue washed with water till the washings were free from ammonia, and then again treated with dilute acetic acid. In the new filtrate the free isocalycanthine was again precipitated with ammonia. This operation yielded 3.5 grams isocalycanthine coming from its hydriodide produced in the reaction. The residue left after the second treatment with the acid consists of the new quaternary iodide. From 10 grams isocalycanthine about 4 grams quaternary iodide were obtained.

It is difficult to explain how from an oxygen-free base containing two atoms of nitrogen in the molecule an oxygen-containing iodide is produced having three atoms of nitrogen in the molecule. It may be that the reaction consists not in a simple methylation, as is usually the case when methyl iodide acts on an organic base, but that the methylation is accompanied by an elimination of an atom of nitrogen as ammonium iodide from two molecules of isocalycanthine under the combined action of the methyl iodide and the oxygen of the air, and that the excess of the fixed base drives out the volatil ammonia from the ammonium iodide, giving isocalycanthine hydriodide. The reaction would then be as follows:

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$$2C_{11}H_{14}N_2 + 2CH_3I + O_2 = C_{24}H_{28}N_3IO.H_2O + NH_4I$$
$$C_{11}H_{14}N_2 + NH_4I = C_{11}H_{14}N_2.HI + NH_3.$$

An indication of formation of ammonia was obtained by placing a strip of moistened red litmus paper under the stopper of the flask in which the reaction took place. After 24 hours' standing the paper was decidedly blue. On the other hand, aside from the not very plausible supposition that methyl iodide would react in such a peculiar way with an organic base,[1] the amount of isocalycanthine hydriodide produced seems to be in excess of what might be expected, considering the amount of quaternary iodide formed. But this discrepancy may be due to the difficulty of quantitatively separating these two substances from each other. The quaternary iodide being considerably less soluble in presence of ammonia than in that of weak acids, undoubtedly dissolves to an appreciable extent in the dilute acetic acid, and is then precipitated by the ammonia together with the free isocalycanthine. The amount of quaternary iodide found is therefore less, while that of free isocalycanthine more than is actually formed in the reaction. As a matter of fact, both the isocalycanthine which remained unchanged, as well as that coming from the hydriodide, contains some of the quaternary iodide. This is easily proved by the presence of iodine in the recovered isocalycanthine and by the yellow color of its solutions in strong acids (see below).

The identity of the isocalycanthine recovered from the reaction products, after purification by solution in acidified water, precipitation with ammonia and recrystallization from a mixture of acetone and water, was established by the melting point, optical rotation and the formation of an insoluble nitrosoamine.

That none of the expected methylisocalycanthine is formed in the reaction is shown by the fact that in the acetic acid solution of the free base isolated from the reaction products, nitrous acid quantitatively precipitates the base as a nitrosoamine. In the filtrate from the nitrosoamine no appreciable amounts of base can be detected by the usual alkaloidal reagents.

That the new reaction product is really a quaternary ammonium salt, not a hydriodide of a secondary or tertiary base, is shown by the fact that ammonia, fixed alkalies and alkaline carbonates simply diminish its solubility in water, but do not precipitate any free base with the removal of hydriodic acid, and that nitrites in neutral solution give a somewhat difficultly soluble crystallin nitrite, while in acid solution no insoluble nitrosoamine is formed.

The new quaternary iodide is both a neutral ammonium salt and a very weak monoacid tertiary base. Itself perfectly colorless and very difficultly soluble in water, it is capable of combining with strong acids to

[1] I have not been able to find an analogous reaction in the literature on alkaloids.

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form readily soluble salts of a fine yellow color. From the yellow solutions of such salts ammonia, fixed alkalies and alkaline carbonates reprecipitate the colorless quaternary iodide. With weak acids no such salts are produced. By means of silver chloride the quaternary iodide can be changed to the corresponding quaternary chloride. The latter is quite soluble in water, and can be used for the preparation of other salts of the quaternary hydroxide underlying the quaternary iodide. All of these salts are colorless, except those with colored acids, like picric and picrolonic. They are all capable of taking up strong acids to form readily soluble salts of a fine yellow color. With weak acids they do not combine. The amount of strong acid taken up by these quaternary salts can be exactly and conveniently determined by titration with standard alkali, using as end point the disappearance of the yellow color. Further addition of alkali has no effect upon them. They all have a neutral reaction towards indicators, are only very slightly colored by weak acids, like acetic, do not react with nitrous acid and do not combine with methyl iodide, though they undoubtedly contain a tertiary nitrogen atom.

Attempts to corroborate the secondary nature of isocalycanthine by acting upon it with ethyl iodide, amyl iodide, benzyl iodide, *o*-xylylene dibromide and benzenesulfochloride were fruitless. In all these cases the free isocalycanthine was quantitatively recovered unchanged.

The quaternary iodide or chloride can be changed by means of silver oxide to the corresponding free quaternary hydroxide. The hydroxide has a strong alkaline reaction and eagerly absorbs carbon dioxide from the air. It could not therefore be prepared in pure condition. On heating the impure hydroxide to about 200–20° in a current of carbon dioxide, it breaks up into two amorphous substances one of which is soluble, the other insoluble, in dilute hydrochloric acid. These will be investigated later.

Experimental.

Having determined the exact nature of the reaction between isocalycanthine and methyl iodide, as described above, the best method for making the new quaternary iodide was found to be a slight modification of the procedure described.

Ten grams crystallized isocalycanthine are boiled under reflux condenser with a mixture of 20 grams methyl iodide and 30 cc. methyl alcohol for about 20 minutes. The alkaloid quickly dissolves in the warm liquid, but very soon heavy crystals begin to separate out, and the boiling mixture commences to bump so violently that it is liable to be thrown out through the condenser. The flask is then detached from the condenser, cooled, stoppered and set aside for four or five days. A large amount of a mixture of white and yellowish, heavy crystals separate out, firmly adhering to

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the sides and bottom of the flask. The supernatant liquid is poured off into a shallow evaporating dish, and evaporated to dryness at ordinary temperature in a good current of air. The crystals in the flask are now added to the small residue in the evaporating dish, and the whole rubbed up with about 20 cc. of concentrated ammonia. The solid material is now almost perfectly white. After standing under cover for 24 hours, the ammoniacal liquid is sucked off, and the crystallin mass washed with water till the washings are free from ammonia. The mass is digested for a few hours with dilute acetic acid (about 6 per cent.), and the acid liquid again sucked off, washing the crystals till the washings are neutral. In the acid filtrate the free isocalycanthine is precipitated with ammonia yielding about 6 grams free alkaloid. The new quaternary iodide left after the treatment with acid and amounting to about 4 grams is recrystallized twice from methyl alcohol and dried at 30° for about 6 hours.

Thus obtained the quaternary iodide forms snow-white, light, soft, glittering, flat needles, insoluble in ether, chloroform and benzene, very difficultly soluble in water, and a little more soluble in alcohol. Of hot methyl alcohol it requires about 30 parts for solution. It turns yellowish on prolonged exposure to the air. It also becomes yellow upon addition of strong acids, but the color is discharged by ammonia, fixed alkali or alkaline carbonates. It contains one molecule of water of crystallization, which it gives off *in vacuo* over drying agents. Hydrated it turns brown at 213–14°, assuming a pasty consistence, but does not melt even at 325° (on Bloc Maquenne). The hydrated salt contained 4 per cent. H_2O. Calculated for $C_{24}H_{28}N_3IO.H_2O$, 3.47 per cent. H_2O.

The analysis of the anhydrous salt gave:

Calculated for $C_{24}H_{28}N_3IO$: I, 25.32; N. 8.39; C, 57.46; H, 5.63
Found: I, 25.52; N, 8.49; C, 57.21; H, 5.96

0.1632 gram of the anhydrous salt dissolved in 100 cc. methyl alcohol (Merck's *pro analysi* and redistilled) gave in 200 mm. tube at 23.5° a rotation of 0.62°. Hence $[\alpha]^{23.5}_{D} = 189.95°$.

Hydriodide of the Quaternary Iodide, $C_{24}H_{28}N_3IO.HI.H_2O$.—Three grams quaternary iodide and 4 grams potassium iodide are dissolved with the aid of heat in a mixture of 10 cc. methyl alcohol and 10 cc. dilute hydrochloric acid (about 10 per cent.). After standing in a cool place for 24 hours the crystals which separated out are washed with a little water and dried at about 40°. Bright yellow, flat silky needles, difficultly soluble in cold solvents, easily soluble in hot water or hot alcohol and insoluble in ether, chloroform or benzene. It gradually turns brown when heated, but does not melt even at 325°.

The water of crystallization is given off *in vacuo* over sulfuric acid. The hydrated salt contained 3.32 per cent. H_2O. Calculated for $C_{24}H_{28}N_3IO.HI.H_2O$, 2.8 per cent. H_2O. The anhydrous salt contained

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40.30 per cent. total I. Calculated for $C_{24}H_{28}N_3IO.HI$, 40.35 per cent. total I.

Quaternary Chloride, $C_{24}H_{28}N_3ClO.3H_2O$.—Fifteen grams of the quaternary iodide are shaken with an excess of freshly prepared silver chloride and about 300 cc. of very dilute hydrochloric acid (about 1.5 per cent.) for half an hour, and the liquid filtered. The clear, deep yellow filtrate is made strongly alkaline with ammonia, which discharges the color immediately, and evaporated to a small bulk. On cooling the whole mass solidifies to a crystallin cake. After washing with a little water the quaternary chloride is dissolved in methyl alcohol, and the solution covered with ether. The crystals which separate out are dried at about 35°. Snow-white, glittering flat needles, easily soluble in methyl alcohol or hot water. Of cold water about 50 parts are required for solution. It turns brown when heated to 214° and melts to a dark liquid at 220°. With gold chloride in presence of sodium carbonate it gives the same intense color reaction as isocalycanthine and calycanthine,[1] but the violet color is not so prompt to make its appearance. The water of crystallization is given off *in vacuo* over drying agents. The anhydrous salt is very hygroscopic. The hydrated salt contained 10.75 per cent. H_2O. Calculated for $C_{24}H_{28}N_3ClO.3H_2O$, 11.01 per cent. H_2O. The anhydrous salt contained 8.82 per cent. Cl. Calculated for $C_{24}H_{28}N_3ClO$, 8.65 per cent. Cl.

0.2705 gram of the anhydrous salt dissolved in 50 cc. water gave in 200 mm. tube at 24° a rotation of 2.67°. Hence $[\alpha]_D^{24} = 246.76$.

Hydrochloride of the Quaternary Chloride, $C_{24}H_{28}N_3ClO.HCl$.—This salt is obtained by dissolving the neutral quaternary chloride in a mixture of methyl alcohol and a little concentrated hydrochloric acid, and covering the solution with ether. It is recrystallized from methyl alcohol covered with ether. Yellow microscopic needles, extremely easily soluble in methyl alcohol, quite soluble in water, insoluble in ether or chloroform. Dried in the air it turns greenish at 155°. On further heating it becomes pasty but does not melt at 250°. For the determination of hydrochloric acid and total chlorine it was dried *in vacuo* over sulfuric acid.

0.1523 gram dissolved in 75 cc. water and titrated with 0.1 *N* KOH to disappearance of yellow color, required 3.4 cc. for neutralization.

Calculated for $C_{24}H_{28}N_3ClO.HCl$, 3.4 cc. 0.1 *N* KOH. The salt contained 16.17 per cent. total Cl. Calculated for $C_{24}H_{28}N_3ClO.HCl$, 15.89 per cent. total Cl.

Attempts to prepare chloroplatinates and chloroaurates of the quaternary base underlying the quaternary iodide were not successful. Neither in acid nor in neutral solution could these salts be obtained. The precipitates produced by adding platinum tetrachloride or gold chloride to

[1] THIS JOURNAL, 27, 153.

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solutions of the quaternary chloride had a strong tendency to pass through the filter, and their color varied with the slightest change in the conditions of preparation. The platinum salt examined under the microscope consisted of a mixture of crystals and amorphous masses.

Quaternary Nitrate, $C_{24}H_{28}N_3O.NO_3$.—The salt is prepared by dissolving the quaternary chloride in hot water and adding a strong solution of potassium nitrate in water. It is recrystallized from boiling water and dried *in vacuo* over sulfuric acid. Snow-white, rectangular prisms, difficultly soluble in cold water, quite soluble in methyl alcohol and hot water. It turns yellowish at 190°, and melts at 192–94° to a reddish liquid.

Calculated for $C_{24}H_{28}N_3O.NO_3$:	C, 66.02; H, 6.47.
Analysis gave:	C, 65.60; H, 6.22.

Quaternary Picrate, $C_{24}H_{28}N_3O.C_6H_2N_3O_7$.—The picrate is prepared by dissolving 2 grams of quaternary chloride in 500 cc. hot water and adding an excess of a hot solution of sodium picrate containing some free sodium carbonate. It is recrystallized from hot water containing some sodium carbonate and dried *in vacuo*. Soft, orange-yellow, oblong plates, difficultly soluble in all solvents tried. It turns reddish at 145° and melts at 155°. The salt contained 13.96 per cent. N. Calculated for above formula, 13.96.

Quaternary Picrolonate, $C_{24}H_{28}N_3O.C_{10}H_7N_4O_5$.—This salt is prepared as follows: Sodium carbonate and picrolonic acid, 1 gram each, are dissolved in 800 cc. warm water, and the solution set aside over night in a cool place. The liquid is filtered, and to the filtrate, heated nearly to boiling, is added a solution of 1 gram of quaternary chloride in 200 cc. hot water. On cooling, most of the picrolonate crystallizes out. It is recrystallized from boiling water, of which it requires about 2000 cc. Bright, orange colored microscopic needles, very difficultly soluble in the usual solvents. Air-dried, it melts at 164–66° to a thick liquid. For the estimation of N it was dried *in vacuo* over sulfuric acid. The salt contained 15.86 per cent. N. Calculated for above formula, 15.38.

The investigation is to be continued.

NORTHWESTERN UNIVERSITY, SCHOOL OF PHARMACY.

NOTE.

Prevention of Bumping.—It is sometimes necessary to boil alcohol out of an aqueous solution which is covered by a layer of specifically lighter oil, as in soap and oil analyses. This is quite difficult to accomplish without loss and is always very tedious on account of the great liability to explosive ebullition.

By introducing a piece of glass tubing open at both ends, the difficulty

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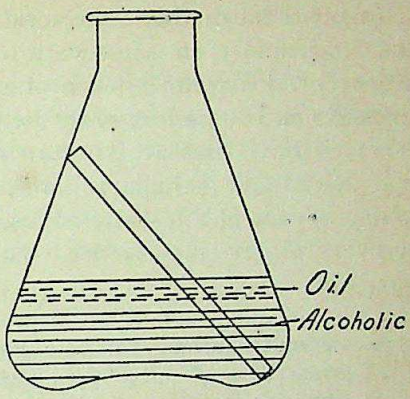
is completely overcome and boiling may be conducted quite rapidly without any loss. The accompanying sketch shows about the proportionate length of tube that is desirable.



If the work is done in a beaker the vessel should be covered by a beaker cover because when boiling is fairly rapid short columns of the alcoholic liquor may be projected up the open tube and lost.

H. SPURRIER.

NEW BOOKS.

The Relations between Chemical Constitution and Some Physical Properties. By SAMUEL SMILES, D.Sc., Fellow of University College, and Assistant Professor of Organic Chemistry at University College, London University. (One of the series of "Text-books of Physical Chemistry" edited by SIR WILLIAM RAMSAY, K.C.B., F.R.S.) London, New York, Bombay and Calcutta: Longmans, Green & Co. 1910. Crown 8vo., pp. xiv + 583. 14s.

This volume is the portliest member of the Ramsay series, so far, at least, as they have yet appeared. Why it has been longer in preparation than have some of the others will readily be understood by any one who considers the extent and variety of the matter that is dealt with. Even so, certain physical properties have been wittingly omitted from consideration; crystallin form would require a separate volume; optical rotatory power, electric conductivity and heat of combustion have been dealt with in other volumes of this series; while solubility, dielectric constant, magnetic susceptibility and other properties have been omitted from discussion as not yet exhibiting sufficiently well defined relationships with chemical constitution to merit special treatment.

The subjects treated are grouped under the heads of capillarity, viscosity, volume relations, specific heat, fusibility, boiling point, refractive and dispersive power, absorption of light, fluorescence, magnetic rotatory power, and anomalous electric absorption. Each of these topics is introduced to the reader by reminding him of the fundamental definitions and groundwork of the subject and of the methods of measurement. The relationships proposed are supported by very many tables, which, as the author points out, are indispensable although detracting from the easy readability of the text. Finally, a clear statement is given in each case of the application that can be made of measurement of each physical property, and thus of its utilitarian value to the research chemist. There are three indexes—of authors, of subjects and of substances.

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In a work like this there may be errors and there may be omissions (as, for instance, in reference to certain work done in this country); the negative value contributed by these, however, is an altogether negligible quantity in comparison with the positive value of the work as a whole. Here we have presented from a modern viewpoint, in English and in a convenient and assimilable form, a collection of relationships and a coherent review of the scattered results of research that must prove a boon to every progressive chemist. This book also should be added to our private libraries. ALAN W. C. MENZIES.

Physico-chemical Tables. Volume 2, Physical and Analytical Chemistry. By JOHN CASTELL-EVANS, F.I.C., F.C.S., Superintendent of the Chemical Laboratories and Lecturer on Inorganic Chemistry and Metallurgy at the Finsbury Technical College. London: Charles Griffin & Company, Limited. Philadelphia: J. B. Lippincott Company. 24x16 cm., xiv + 686 pp. $12.00 net.

The first volume of this work appeared in 1902, and has already been reviewed in these pages (THIS JOURNAL, **25**, 657 (1903)). The present volume continues Part III, "Physics," embraces the whole of Part IV, "Analytical Chemistry," and contains a few pages of Supplementary Tables of Weights and Measures based on the relative values of metric and imperial units as legally fixed in 1907 by the Board of Trade from the results of careful comparison of the standards.

The tables in Part III are divided into four groups: The first of these, *Molecular Dynamics*, embraces tables of such constants as molecular speeds, free path and molecular magnitude in gases; speed of sound in various media; viscosity of gases; viscosity of liquids, mixed liquids, and solutions (73 pp.); molecular volumes of liquids and vapors, etc. The second group, *Capillarity and Surface Tension*, contains tables of the values of these constants for various liquids, with their relation to temperature, and similar data for solutions and for fused substances. Later pages tabulate relationships of surface tension with other physical properties and with chemical constitution. The third group, *Physical Properties of Solutions*, contains tables of the boiling points of various aqueous solutions (11 pp.), followed by extensive tables of specific gravity of solutions, chiefly aqueous (113 pp.). Then follow tables of solubility in water (32 pp.) and in alcohol, solubility data for "mixed solutions and solutions in mixed solvents," etc. The fourth group of tables in Part III, *Molecular Weights*, contains values for molecular freezing point depression and boiling point elevation as calculated and as observed; and tables of the lowering of vapor pressure of water and of mercury due to the presence of a solute.

Part IV, "Analytical Chemistry," contains an assortment of tables whose character is sufficiently indicated by the heading. In the com-

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putation of analytical factors, the International Atomic Weight Table of 1904 was used.

It is indeed fortunate that the late Dr. Castell-Evans was able to complete this work, for which English-speaking chemists and physicists must alike stand in his debt. The statistical temperament in such a high degree is not given to many. For the collection of such data in the future, however, we are able to look forward to the International Annual Table of Constants beginning from 1910. Time must test the accuracy of quotation and recalculation of Castell-Evans's work; but, however the test may result, it must be true for this, as for the earlier volume, that the searcher will often here be led to data which were missed in other tables. Verification by reference to the original literature must follow in any case, and it is to be regretted that the references given in this work are not more complete. Some may think that the instinct for tabulation has sometimes led the author rather too far: for example, whenever called upon to titrate with columbium pentafluoride, many analysts might prefer to spend some moments in computing their own analytical factors from the atomic weight table of 1911 rather than to turn up the factor here tabulated (to *seven* places of logarithms) from the atomic weights of 1904. Any minor blemishes, however, will be gladly overlooked in view of the undeniable value of the work as a whole. In the absence, especially, of any large text-book of physics, works of this character in English have been all too few.

ALAN W. C. MENZIES.

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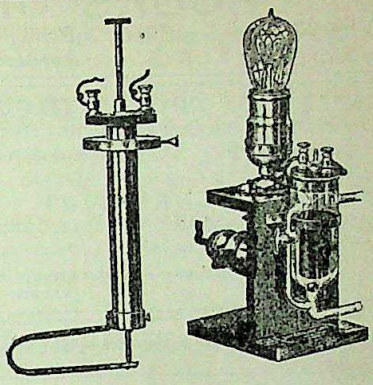

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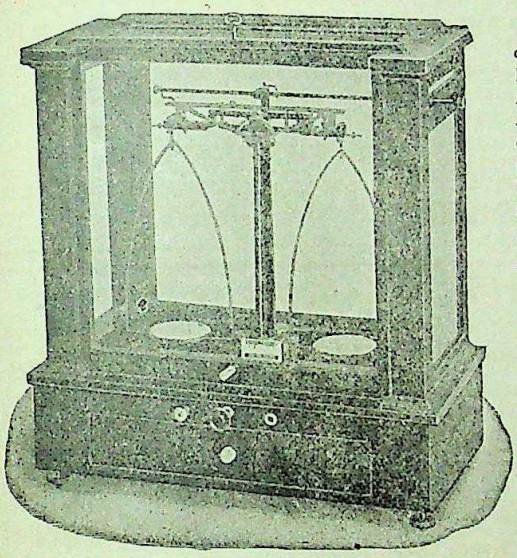

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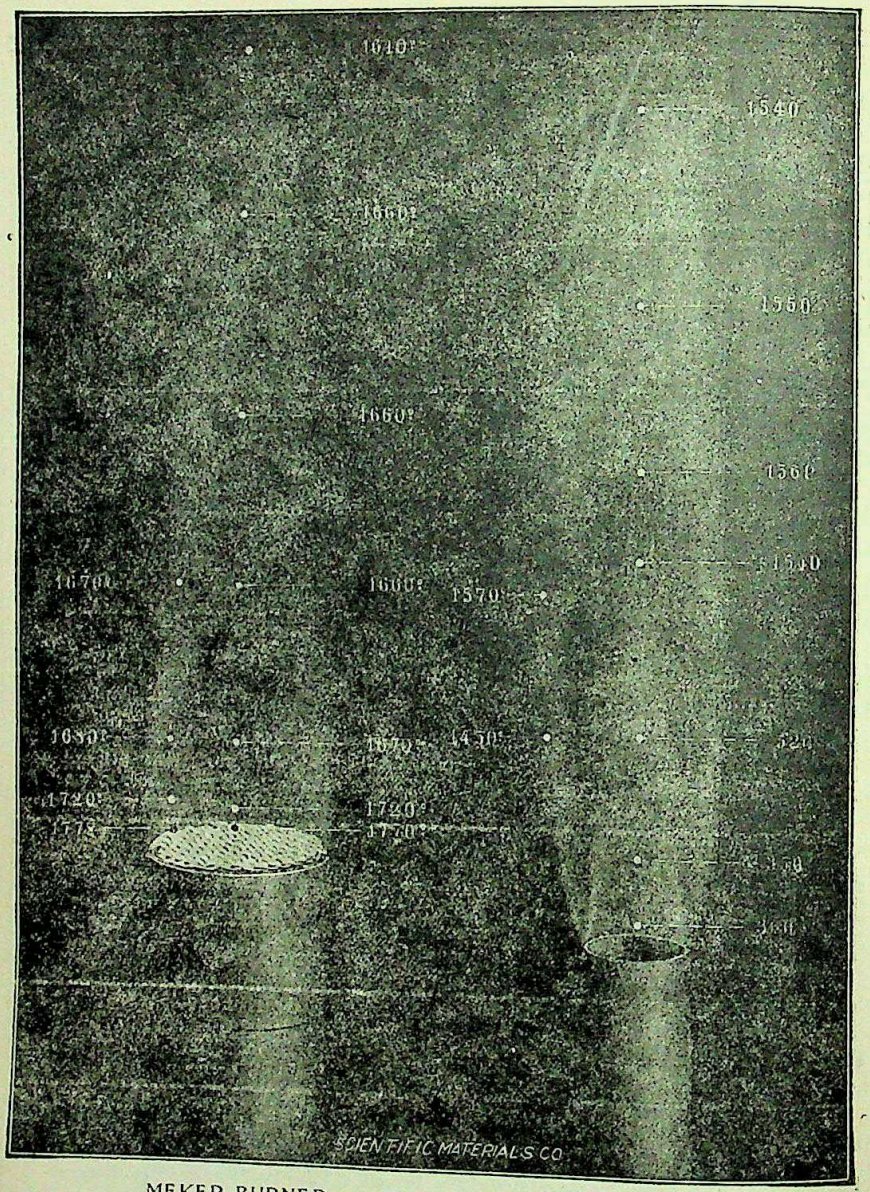

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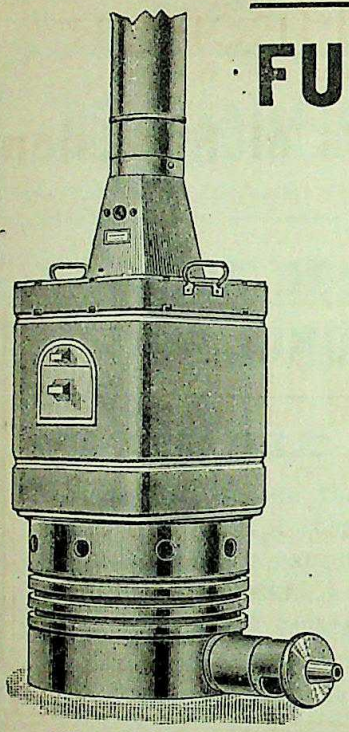

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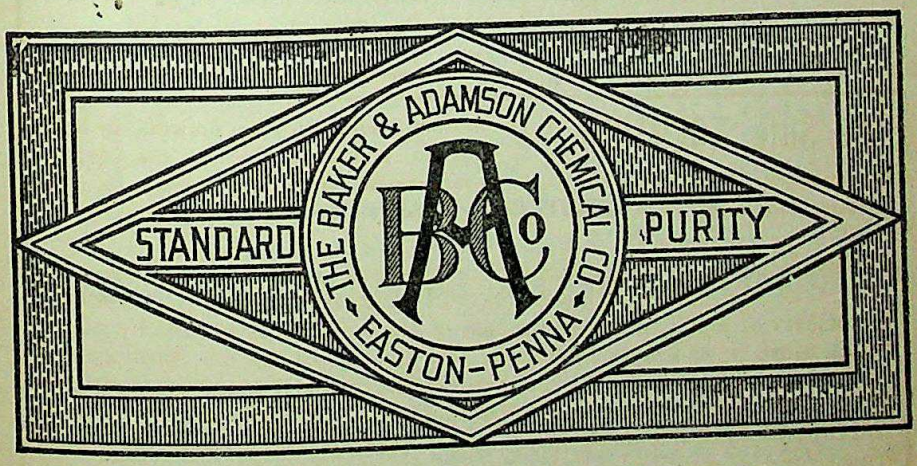

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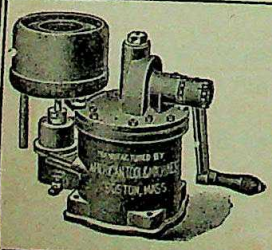

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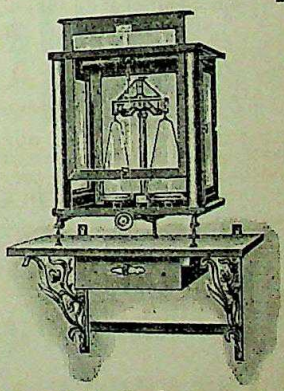

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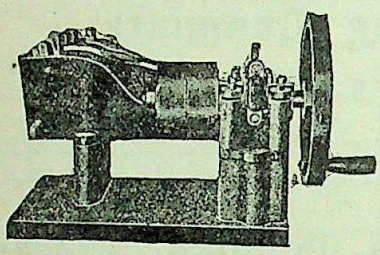

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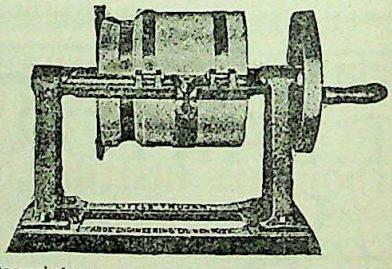

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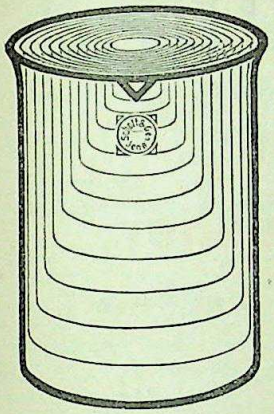

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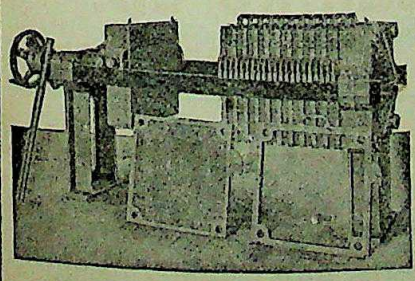

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ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY. Vol. VII, 1910. 5¾x8½, 303 pp. $2.00.

d'ALBE, E. E. F. Contemporary Chemistry. A survey of the present state, methods and tendencies of chemical science. 5½x8¼, 188 pp.

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Issued with the November Number, 1911.

Proceedings.

COUNCIL.

The following letter ballot was sent to the Council on September 5th:

AMERICAN CHEMICAL SOCIETY.

DURHAM, N. H., Sept. 5, 1911.

COUNCIL OF THE AMERICAN CHEMICAL SOCIETY.

Gentlemen:

At the Indianapolis meeting an invitation asking the American Chemical Society to join the International Association of Chemical Societies, the preliminary organization of which had been undertaken by representatives of the English, German and French societies, was submitted. The following resolution was passed:

The American Chemical Society views with favor the proposal to join with the chemical societies of London, France and Germany in the formation of an international association on the lines suggested in the provisional program forwarded by Professor Ostwald, and the President of the American Chemical Society is hereby empowered to enter into correspondence on the details of the proposed organization.

In accordance with this action the President has corresponded with Professor Ostwald and it is estimated that the share of the American Chemical Society in the general office expenses will amount to about $100.00 a year.

In order that plans for commissions to study the nomenclature of organic and inorganic chemistry and other important matters be set in motion, the International Association earnestly desires that we quickly communicate our intention to join and name our three delegates. President Smith feels that he has no authority to proceed under the motion as above stated and I, accordingly, submit to you the following resolution:

Resolved, That the American Chemical Society join the International Association of Chemical Societies and that the President be empowered to appoint the three delegates to represent our Society on the Council.

To be counted, your ballot must reach me on or before September 26th.

CHARLES L. PARSONS, *Secretary*.

The ballot was counted by a committee consisting of G. A. Perley, C. F. Whittmore and S. H. Katz and resulted—75 in favor of the resolution to 1 opposed.

As a result of the above vote, President Smith has appointed T. W. Richards, W. A. Noyes and A. L. Day as delegates of the American Chemical Society to the Council of the International Association of Chemical Societies.

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President Smith has also made the following appointments:

Delegates to the National Conservation Congress at Kansas City.—E. H. Keiser, S. Avery, Sidney Calvert, E. H. S. Bailey, H. E. Barnard.

Delegate to the American Mining Congress, Chicago.—Charles L. Parsons.

Members of the Perkin Medal Committee.—Willis R. Whitney, W. H. Walker, W. D. Richardson, A. D. Little, F. B. Carpenter, William Brady.

Committee to Consider the Question of a Code of Professional Ethics for Chemists, to report to the Industrial Division at the Washington meeting.—A. C. Langmuir, C. F. McKenna, Lucius P. Brown.

The following have been appointed as officers of the Biological Section for the Washington meeting: Carl S. Alsberg, Chairman, Bur. of Plant Industry, Washington, D. C.; I. K. Phelps, Secretary, Bur. of Chemistry, Washington, D. C.

The following have been appointed as officers for the Section on the Chemistry of India Rubber for the Washington meeting: D. A. Cutler, Chairman, care of Rubber Goods Mfg. Co., 42 Broadway, New York City; F. J. Maywald, Secretary, 89 Pine St., New York City.

President Smith has added A. C. Fieldner to the Joint Committee on Coal Sampling and Analysis.

CHARLES L. PARSONS, *Secretary.*

BOARD OF DIRECTORS.

The Directors met at the Chemists' Club, New York City, on the evening of Tuesday, September 26, 1911, with President Smith in the chair and Directors Bogert, Love, Hallock, Parsons and Parker present.

A letter from the Secretary of the Industrial Division was read announcing a vote of that Division requesting the Directors to appoint a committee to consider the question of the need of a professional code of ethics among chemists and to report at the next meeting of the Division. The Directors, deeming that they had no power in the matter, voted that the matter of the appointment of the committee be referred to President Smith.

A second communication from the Industrial Division was presented to the effect that the Division of Industrial Chemists and Chemical Engineers recommend to the attention of the Directors of the American Chemical Society the advance publication and circulation of certain papers in order to bring out discussion and that they further suggest the desirability of having the discussions reported accurately. On vote of the Directors the Secretary was instructed to write to the Division of Industrial Chemists and Chemical Engineers that the state of the finances of the Society does not admit of the printing of papers in advance of the meet-

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ings, the employment of reporters to take down discussions, or the printing of the discussions if they could be reported, as the funds of the Society now barely meet the cost of our journals and administration, but that the Directors heartily approve the policy if the Division can bear the expense from its own funds.

It was voted that the action of the Secretary in transferring the employment advertisements from the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY to the *Journal of Industrial and Engineering Chemistry* on request of Editor Whitaker and the concurrence of Editor Noyes be approved.

It was voted that the question of disposing of the remaining library stacks from the library at the former Chemists' Club be referred to E. G. Love with power.

It was voted that the appropriation to *Chemical Abstracts* for the present fiscal year be increased by a sum not to exceed $1800.

It was voted that the appropriation to the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY for the present fiscal year be increased by an amount not to exceed $1000.

It was voted that the appropriation to the *Journal of Industrial and Engineering Chemistry* for the present fiscal year be increased by an amount not to exceed $2500.

The Editor of the *Journal of Industrial and Engineering Chemistry* having presented a statement that the paper of the present journal is entirely unsuitable for cuts, that the insertion of specially covered paper for cuts involves entirely unnecessary expense and that advertisements could not be secured for the Journal unless a different kind of paper was used, it was voted that the question of paper for the *Journal of Industrial and Engineering Chemistry* for the year 1912 be referred to the Editor of that journal with power under the limitation that the cost of paper shall not be increased.

It was voted that inasmuch as the visible income of the Society for the year 1912 is fifteen thousand dollars less than the funds asked for in the preliminary estimates of the officers of the Society to meet the expenses of the Society for that year, the Secretary be instructed to write to the various officers of the Society calling their attention to the necessity of limiting their expenditure the coming year to the lowest possible amount and that they be asked to send in a revised estimate to the Secretary of the Society.

In view of the fact stated in the foregoing vote, and inasmuch as the chief object of the Society must continue to be the publication of original articles, it is evident that the funds of the Society will not permit any increase in the size of *Chemical Abstracts* for the year 1912. It was voted, therefore, that the Secretary be instructed to ask the Editor

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of *Chemical Abstracts* to consult with his associate editors and departmental heads and to report to the Directors, in advance of their final consideration of the budget, some plan for limiting the expenses of the coming year to an amount not exceeding that expended during 1911.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary.*

MEMBERS ELECTED BETWEEN SEPTEMBER 15TH AND OCTOBER 15TH.

Buhrman, Robert L., 425 Purcell Ave., Cincinnati, Ohio.
Cabot, Samuel, 141 Milk St., Boston, Mass.
Chen, Huang, 116 University Station, Urbana, Ill.
Follin, E. E., Port Edwards, Wisc.
Goldschmidt Detinning Co., Chrome, N. J.
Hogan, F. W., Brentwood, Tenn.
Kitchen, Harry C., 416 Federal Bldg., Indianapolis, Ind.
Latimer, Charles A., 1135 Main St., Grand Junction, Colo.
Lee, Victor P., 1705 Grand Ave., Nashville, Tenn.
Lindsay, Charles T., cr. Union Metallic Cartridge Co., Bridgeport, Conn.
McConnell, Glenver, 133 Lincoln Ave., Grove City, Penna.
McGregor, Clark M., Heilwood, Penna.
Minor, Roddie, 512 West 136th St., New York City.
Moses, Herbert L., 2344 Eutaw Place, Baltimore, Md.
Niagara Alkali Co., Niagara Falls, N. Y.
Niven, Maxim, 31 Elm St., Rochester, N. Y.
Parker, Vilas, 524 Woodbine Ave., Oak Park, Ill.
Phillips, W. E., 45 Ben Lamond Ave., East, Toronto, Canada.
Pittenger, Paul S., 426 So. 13th St., Philadelphia, Penna.
Plummer, James K., Raleigh, No. Car.
Powell, Sheppard T., 102 W. Fayette St., Baltimore, Md.
Ralston, Oliver C., 226 W. Eighth St., Leadville, Colo.
Rattle, Wm., Jr., Commercial Bank Bldg., Cleveland, Ohio.
Schmidt, H. E., 1426 Chestnut St., Terre Haute, Ind.
Schott, Otto, Fifth Ave. Bldg., New York City.
Schrenkeisen, Raymond M., 1070 Madison Ave., New York City.
Sergeant, E. M., cr. Niagara Alkali Co., Niagara Falls, N. Y.
Shaw, Jos. A., 3210 Elsinore Square, Pittsburg, Penna.
Stoppel, Ernest A., Bureau of Standards, Washington, D. C.
Suchy, A., cr. Niagara Alkali Co., Niagara Falls, N. Y.
Traill, Robert J., 106 Mansfield St., Montreal, Canada.
von Planck, Gordon L., Pittsburg, Calif.
Whitcomb, Emmons J., 358 Broadway, Winter Hill, Mass.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

SYRACUSE MEETING.

The annual meeting of the Section, which was also the occasion of

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the annual outing, was held on Saturday, June 24th, at Owasco Lake, N. Y. The following officers were elected: *President*, H. Monmouth Smith; *Vice-President*, Edward S. Johnson; *Secretary*, Geo. M. Berry, care Halcomb Steel Co., Syracuse, N. Y.; *Treasurer*, Arthur G. Carman; *Local Councilor*, to serve until 1914, Darwin A. Morton.

GEORGE M. BERRY, *Secretary*.

CINCINNATI SECTION.

The one hundred and seventieth regular meeting of the Section was held Wednesday evening, Sept. 20th, in the Chemistry lecture room of the University of Cincinnati. Paul H. Smyth read his thesis entitled "The Output of the Cupola," for which he received the Hochstetter prize. Drs. Jones, Goettsch and Bye gave an account of the Indianapolis meeting.

B. M. PILHASHY, *Secretary*.

CALIFORNIA SECTION.

The fifty-eighth regular meeting was held on Saturday evening, September 23d, at 8 o'clock, at Bergez & Franks' Café, preceded by the usual dinner. The paper of the evening, "The Problem of Employment," was presented by A. Vekander.

CHARLES S. ASH, *Secretary*.

SECTION OF EASTERN NEW YORK.

The September meeting was held in Schenectady at the Chemical Laboratory of Union College, on Friday, September 29th, at 8.15 P.M. Dr. C. F. Hale, Professor of Physics at the Albany Normal College, gave a talk on "The Measurement of Very Small Gas Pressures."

The regular meeting for October was held at the Sage Laboratory of Rensselaer Polytechnic Institute, Troy, on Friday evening, October 20th, at 8.15 o'clock. The following paper was presented: "Reductions with Metallic Sodium," by Dr. M. A. Hunter.

G. R. FONDA, *Secretary*.

SECTION OF WESTERN NEW YORK.

A general meeting of the Section was held on October 3rd, at 8.30 P.M., in the lecture hall of Buffalo University, Buffalo, N. Y., preceded by an informal dinner at the German-American Hotel.

Papers were read by Mr. W. H. Watkins, "Is Chemistry a Failure?" and Prof. A. P. Sy, "A Résumé of 950 Judgments against Food Adulterators."

WALTER WALLACE, *Secretary*.

NEW YORK SECTION.

The first regular meeting of the session of 1911–12 was held in Rumford Hall on Oct. 6th, Dr. A. C. Langmuir in the chair. The program was as follows: "Some New Theories of Physics" and "Demonstration of a Laboratory Still for Quantitative Distillation with Steam in Vacuum," by A. C. Langmuir, Chairman. "The Sodium Chloride Contents of Milk," by Paul Poetschke.

C. M. JOYCE, *Secretary*.

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ST. LOUIS SECTION.

A joint meeting of the St. Louis Section of the American Chemical Society and the St. Louis Chemical Society was held on Monday evening, October 9th, at the Academy of Science Building, at eight o'clock.

Mr. J. J. Kessler gave two short papers: "The Iodine Number and Titre Test of Oil Mixtures," and "The Determination of Antimony in Babbitt Metal." There was also some discussion of the Indianapolis meeting of the American Chemical Society. GEO. W. WALLACE, *Secretary.*

WASHINGTON SECTION.

The two hundred and eighth regular meeting was held in the Assembly Room of the Cosmos Club, Thursday, October 12th, at 8 P.M. The following program was presented:

"A New Vacuum Sublimation Apparatus," Geo. W. Morey (Bureau of Standards). "Creatinine in Soils," E. C. Shorey (Bureau of Soils). "The Origin of Creatinine in Soils," M. X. Sullivan (Bureau of Soils). "The Effect of Creatinine in Growth," J. J. Skinner (Bureau of Soils). "A New Bromine Method for the Determination of Aromatic Phenols—Its Special Application to Thymol," Atherton Seidell (Hygienic Laboratory).

H. S. BAILEY, *Secretary.*

CHICAGO SECTION.

The October meeting was held in the rooms of the Western Society of Engineers, on Friday evening, October 13th, at 8.00 P.M., preceded by an informal dinner at Kuntz-Remmler's. The papers of the evening were:

"Present Day Glass Conditions," Henry W. Hess, Libbey Glass Co., Toledo, Ohio. "Illumination and Some Effects of Glass on Same," Chandler R. Gilman, Chief Electrician, C. M. & St. P. R'y Co., Milwaukee, Wis.

D. K. FRENCH, *Secretary.*

NORTHEASTERN SECTION.

The one hundred and third regular meeting of the Section was held Friday, October 20th, at eight P.M., at the Twentieth Century Club, Boston, preceded by dinner at 6.30.

Dr. Arthur M. Comey, Director of the DuPont Research Laboratories in Chester, Pa., addressed the Section on "The Testing of High Explosives."

WARREN K. LEWIS, *Secretary.*

DECEASED MEMBERS.

Isaac Adams, North Cambridge, Mass.
Dr. Wm. H. McLauchlan, Syracuse, N. Y.
Wm. A. A. Reinhardt, Baltimore, Md.

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VOL. XXXIII. NOVEMBER, 1911. No. 11.

THE JOURNAL

OF THE

American Chemical Society

ANNUAL REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS, 1912.

Received October 11, 1911.

Since the report of the Committee for 1911 was prepared, a number of important determinations of atomic weight have been published, which may be summarized as follows:

Nitrogen.—Guye and Drouginine,[1] from seven analyses of N_2O_4, find, in mean, N = 14.010.

Sulfur.—Burt and Usher,[2] by analysis of nitrogen sulfide, N_4S_4, have determined the ratio S : N : : 1.0 : 0.43687. Hence, calculating with N = 14.009, S = 32.067; in good agreement with the accepted value.

Chlorine.—Burt and Gray[3] have continued their work upon the density of hydrochloric acid, and confirmed their former determination of Cl = 35.46.

Iodine.—Baxter[4] has redetermined the ratio of iodine to silver with extreme care. Combining his results with the previously determined ratio of silver to iodine pentoxide he finds Ag = 107.864 and I = 126.913. The value for silver varies from that found by Richards and Willard, and the discrepancy is as yet unexplained.

Sodium.—Goldbaum[5] has made analyses of sodium chloride and bromide by a new electrolytic method. The salts were electrolyzed with a mercury cathode and a weighed silver anode, and on the latter the halogen was collected in weighable form. From the chloride, with Cl = 35.458,

[1] *J. chim. phys.*, 32, 513.
[2] *Proc. Roy. Soc.*, 85A, 82.
[3] *Chem. News*, 103, 161, 170.
[4] THIS JOURNAL, 32, 1591.
[5] *Ibid.*, 33, 35.

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Goldbaum found Na = 22.997; the bromide, with Br = 79.920, gave Na = 22.998.

Calcium.—Two papers by Richards and Hönigschmid[1] on the atomic weight of calcium have appeared. From analyses of calcium bromide, Ca = 40.070, when Ag = 107.88. From analyses of the chloride, Ca = 40.074. The value 40.07 is adopted in the table at the end of this report.

Cadmium.—Perdue and Hulett,[2] from electrolytic analyses of cadmium sulfate, conclude that the atomic weight of cadmium is near 112.30. This is lower than the accepted value; but as the investigation is being continued with other salts of cadmium, any change in the table should be deferred.

Mercury.—Easley[3] has continued his work on the atomic weight of mercury, varying his methods. New analyses of the chloride give Hg = 200.63, in confirmation of his former determinations. In a private communication he states that analyses of the bromide lead to the same value. The new figure, Hg = 200.6, should be adopted.

Vanadium.—McAdam,[4] by reducing sodium vanadate to sodium chloride, by heating in a stream of dry hydrochloric acid, finds V = 50.967, or 51, in round numbers. The latter figure is as probable as any.

Tantalum.—Balke,[5] by hydrolysis of tantalum pentachloride, has determined the ratio $2TaCl_5 : Ta_2O_5$. The mean of five concordant determinations gives Ta = 181.52, when Cl = 35.46. The rounded-off value 181.5 should be accepted.

Tellurium.—Flint[6] has continued the work reported by Browning and Flint in 1909 on the fractionation of tellurium by hydrolysis of the tetrachloride. With successive fractions the atomic weight steadily decreased. Seven analyses of the basic nitrate representing the tenth fractionation gave values for Te ranging from 124.25 to 124.42. As the work is still in progress, any acceptance of these low figures would be premature.

Iron.—Baxter, Thorvaldson and Cobb,[7] from analyses of ferrous bromide, find Fe = 55.838 when Ag = 107.88. In another communication[8] Baxter and Thorvaldson find Fe = 55.836. The latter figure is the mean of two series, *meteoric* iron being taken as the starting point. The value 55.84 is given in the table.

[1] THIS JOURNAL, 32, 1577; 33, 28.
[2] *J. Physic. Chem.*, 15, 155. See also Richards, THIS JOURNAL, 33, 1888.
[3] THIS JOURNAL, 32, 1117.
[4] *Ibid.*, 32, 1603.
[5] *Ibid.*, 32, 1127.
[6] *Am. J. Sci.*, [4] 30, 209.
[7] THIS JOURNAL, 33, 319.
[8] *Ibid.*, p. 337.

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Uranium.—Oechsner de Coninck,[1] by reduction of UO_2Cl_2 and $UO_3.H_2O$ to UO_2 in hydrogen, concludes that U = 238.5. The work is only approximate in character.

Scandium.—Meyer and Winter,[2] in a preliminary series of experiments, find values for Sc ranging from 44.86 to 45.37; in mean, 45.12. This is higher than the recognized value, but its adoption would be premature. More details are needed.

Neodymium.—By extended and careful analyses of the chloride, Baxter and Chapin[3] have redetermined the atomic weight of neodymium. From the ratio $NdCl_3 : 3Ag$, Nd = 144.268. From the ratio $NdCl_3 : 3AgCl$, Nd = 144.272. A small correction raises the value to 144.275. The rounded-off value 144.3, given in the table, may be properly retained.

Erbium.—Hofmann,[4] from analyses and syntheses of the sulfate of "neo-erbium," finds Er = 167.68. This may be rounded to 167.7.

Argon.—Determinations of the density of argon, by Fischer and Froboese,[5] give a mean value of 19.95. Hence A = 39.90.

Niton.—Gray and Ramsay,[6] with the aid of the microbalance, have determined the density of the gaseous emanation from radium, to which they give the name *niton*. The mean value found gives Nt = 223, but the value 222.4 is preferred. The gas is a member of the argon group, and seems to be entitled to recognition in the table. Debierne,[7] by a different method, has found the value 220 for the emanation, which is in fair agreement with the determination by Gray and Ramsay.

The table of atomic weights for 1912 follows.

In accordance with a suggestion received from Germany, the changed values are indicated by an asterisk. The changes are few in number, and only in two cases are they large.

NOTE.—The publication of this report has been unavoidably delayed by the difficulties of correspondence between the widely separated members of the committee. Since it was written, several noteworthy papers upon atomic weights have appeared. Harcourt and Baker have thrown doubt upon Flint's work relative to tellurium. Staehler and Meyer have investigated the ratio $KClO_3$ to KCl. There are also papers upon holmium, by Holmberg, on iridium by Hoyermann, on selenium by Kuzma and Krehlik, and on tantalum by Chapin and Smith. F. W. C.

[1] *Compt. rend.*, 152, 711 and 1179.
[2] *Z. anorg. Chem.*, 67, 398.
[3] *Proc. Am. Acad.*, 46, 215.
[4] *Ber.*, 43, 2635.
[5] *Ibid.*, 44, 92.
[6] *Proc. Roy. Soc.*, 84 A, 536.
[7] *Compt. rend.*, 151, 126.

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International Atomic Weights, 1912.

	Symbol.	Atomic weight.
Aluminium	Al	27.1
Antimony	Sb	120.2
Argon	A	39.88
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.92
Cadmium	Cd	112.40
Caesium	Cs	132.81
*Calcium	Ca	40.07
Carbon	C	12.00
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.5
Copper	Cu	63.57
Dysprosium	Dy	162.5
*Erbium	Er	167.7
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	69.9
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	3.99
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
*Iron	Fe	55.84
Krypton	Kr	82.92
Lanthanum	La	139.0
Lead	Pb	207.10
Lithium	Li	6.94
Lutecium	Lu	174.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
*Mercury	Hg	200.6
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.2
Nickel	Ni	58.68
*Niton (radium emanation)	Nt	222.4
Nitrogen	N	14.01
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Praseodymium	Pr	140.6
Radium	Ra	226.4
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	44.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulphur	S	32.07
*Tantalum	Ta	181.5
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.4
Thulium	Tm	168.5
Tin	Sn	119.0
Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	238.5
*Vanadium	V	51.0
Xenon	Xe	130.2
Ytterbium (Neoytterbium)	Yb	172.0
Yttrium	Yt	89.0
Zinc	Zn	65.37
Zirconium	Zr	90.6

Signed,

F. W. CLARKE,
T. E. THORPE,
W. OSTWALD,
G. URBAIN.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 72.]

THE EFFECT OF SALTS ON THE SOLUBILITY OF OTHER SALTS. I.

BY ARTHUR A. NOYES AND WILLIAM C. BRAY.

Received September 22, 1911.

A. INTRODUCTION.
B. PRELIMINARY NOTE ON THE EFFECT OF SALTS ON THE SOLUBILITY OF UNI-BIVALENT SALTS.

A. Introduction.

It is the purpose of the following articles to describe the researches on the effect of salts on the solubility of other salts, which have been in progress in this laboratory for a number of years with the object of investigating the principles underlying this phenomenon. These investigations were carried out in large part with the aid of grants from the Carnegie Institution of Washington, to which we wish to acknowledge our great indebtedness.

The following well-known solubility principles were originally formulated upon the basis of the law of mass action:

I. The product of the concentration of the ions of a salt present as solid phase has the same value in dilute solutions of other salts as it has when it is present alone.[1]

II. The concentration of the un-ionized portion of a salt present as solid phase has the same value in dilute solutions of other salts as it has when present alone.[2]

It was, however, early recognized that both of these principles can not hold true accurately, since the ionization of salts (as derived from the conductance-ratio or freezing-point lowering) does not change with the concentration in accordance with the law of mass action. The first one has been generally employed, since it was shown by Arrhenius[3] that the second of the above principles is not even approximately true. Thus with the aid of his own data on the effect produced on the solubility of certain silver salts of organic acids by salts with a common ion, he found that the concentration of the un-ionized portion decreased rapidly with increasing ion-concentration, in some cases to such an extent that the total solubility became less than the concentration of the un-ionized portion in pure water. From a further study of the same data, Stieglitz[4] concluded that the first principle expressing the constancy of the product of the ion-concentrations is approximately true for these uni-univalent silver salts, and suggested that this might be adopted

[1] Nernst, *Z. physik. Chem.*, 4, 379 (1889).
[2] A. A. Noyes, *Ibid.*, 6, 243 (1890).
[3] Arrhenius, *Ibid.*, 31, 224 (1899).
[4] Stieglitz, THIS JOURNAL, 30, 946 (1908).

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for the present as an approximate empirical principle. Recent computations have shown, however, that the first principle is also subject to considerable deviations, and that these lie in a direction opposit to that of the deviations from the second principle. Thus, it has been computed[1] that in a solution saturated at 40° both with thallous chloride and thiocyanate, where the total concentration is about 0.04 normal, the concentration of the un-ionized TlCl is about 15 per cent. less, and the product of the concentration of the Tl^+ and Cl^- ions about 5 per cent. greater than it is in a solution of thallous chloride alone.

Any such computations necessarily involve some principle in regard to the ionization of salts in mixtures. Assuming that the conductance-ratio Λ/Λ_0 is an accurate measure of ionization, the following principle, first stated by Arrhenius,[2] has been well established in the case of uni-univalent salts through the study of the conductance of mixtures of them:[3] In a mixture of two salts with a common ion each salt has a degree of ionization equal to that which it has when alone present in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture. This principle when combined with the empirical law, which has been found to express the change of the ionization $\gamma = \Lambda/\Lambda_0$ of single salts, with the concentration (C),

$$(C\gamma)^n/C(1-\gamma) = K \qquad (1)$$

may be expressed mathematically by the following equation:[4]

$$C_{B+}C_{A-}/C_{BA} = K(\Sigma C_i)^{2-n} \qquad (2)$$

where K is a constant characteristic of the salt, C_{B+} and C_{A-} are the concentrations of the positive and negative ions, of a salt BA, C_{BA} that of the un-ionized portion of the salt, and ΣC_i denotes the sum of the equivalent concentrations of all the positive or negative ions present in the solution, a quantity which will hereafter be called the total ion-concentration. The exponent n has a value lying almost always between 1.40 and 1.60.

In applying this equation (2) to any special mixture the values of γ, ΣC_i, n and K are first determined for each salt from the conductance data for the salt, and the values of C_{B+}, C_{A-} and C_{AB} for each salt in the mixture and of ΣC_i are then computed from the equation by a method of approximation.[5] In mixtures with a common ion it is only necessary to know the relation between γ and ΣC_i for each salt, since the above ionization rule may then be applied directly. In mixtures without a common ion the relation of the function $C_{B+}C_{A-}/C_{BA}$ to

[1] Noyes, *Tech. Quart.*, 17, 305 (1904); *Z. physik. Chem.*, 52, 636 (1905).
[2] *Z. physik. Chem.*, 2, 285 (1888); 31, 218 (1899).
[3] For references see Sherrill, This Journal, 32, 741 (1910).
[4] Arrhenius, *Z. physik. Chem.*, 31, 218 (1899). Sherrill, *Loc. cit.*
[5] For examples see This Journal, 32, 741 (1910); 31, 754 (1909).

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ΣC_i is determined for the separate salts, and is then applied for calculating the concentrations in the mixture.

It is important to note that the only evidence in favor of equation (2) is that the specific conductances of mixtures calculated with its aid are in good agreement with the experimental values. It therefore will furnish correct values of the ion-concentrations only in case the commonly accepted principle is correct, that the conductance ratio Λ/Λ_0 is a reliable measure of the degree of ionization of a single salt, a principle which can be true only in case the mobilities of the ions do not vary with the concentration.

In the case of salts of the uni-bivalent type, there is, furthermore, the uncertainty as to whether intermediate ions (such as KSO_4^- or NO_3Ba^+) are present in considerable proportions. Certain remarkably simple principles have, however, been established, which have been thought to indicate that the complications which would arize from ionization in two successive stages do not exist. Namely: 1. The conductance-ratio of such salts changes with the concentration according to the same exponential law (expressed by equation (1) above) that holds in the case of uni-univalent salts.[1] 2. The conductance of mixtures of such salts can be approximately calculated from the conductance of the constituents by the same principle (expressed by equation (2)) that holds for uni-univalent salts.[2] 3. The transference numbers of uni-bivalent salts (except those of the bivalent metal halides) change only slightly with increasing concentration.[3] 4. Simple mixed salts (such as $BaClNO_3$) scarcely ever separate in the solid state when solutions of the constituent salts are evaporated. In view of these facts we have assumed provisionally, in this first discussion of the data, that intermediate ions do not exist and that the concentration of the ions and of the un-ionized portion of uni-bivalent salts, whether present alone or in mixtures, can be calculated with the help of the same principles as are applicable to uni-univalent salts. The hypothetical character of this assumption is, however, fully recognized, and it is hoped that the nature of the results in the case of uni-bivalent salts will throw some light upon this question.

[1] Cf. Noyes, Melcher, Cooper and Eastman, THIS JOURNAL, 30, 335 (1908). Noyes and Johnston, THIS JOURNAL, 31, 987 (1909).

[2] Cf. Noyes, *Tech. Quart.*, 17, 293 (1904); *Science*, 20, 584 (1904); *Z. physik Chem.*, 52, 635 (1905). Sherrill, *Loc. cit.*

[3] Cf. Falk, THIS JOURNAL, 32, 1569 (1910). It should be noted that this author mentions a hypothesis, suggested by Lewis, which requires that the intermediate ion have such a conductance that its presence would not influence the value of the transference number. Under this hypothesis the conductance of the intermediate ion is in general much smaller than that of the corresponding bivalent ion. It follows from this that the concentration of the univalent ion calculated as usual under the assumption that no intermediate ion is present would be too small.

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By applying the above principles, there have, accordingly, been calculated in this series of papers the concentration of the un-ionized portion and the product of the concentration of the ions of the salt with which the solution is saturated, and in this way the character and magnitude of the deviations from the two solubility principles derived from the mass-action law have been determined.

In dealing with these deviations, it is convenient to make use of the concept of *activity*, proposed by Lewis.[1] Without citing the fundamental definitions of this quantity, or its thermodynamic relations to other quantities, it will suffice for our purpose to state that the activities of a substance in two phases in equilibrium with each other are equal, that activity has the same dimensions as concentration, and that the activity of each substance in any solution always has such a value that all mass-action relations are valid. Thus in any aqueous or non-aqueous solution in equilibrium with the solid salt BA, the two solubility principles are necessarily true, when expressed in activities:

$$A_{B+} \times A_{A-} = \text{const. and } A_{AB} = \text{const.}$$

For each substance in solution, as the concentration is decreased, the ratio of activity to concentration, the *activity coefficient* (A/C), approaches a constant value, which in aqueous solutions may for convenience be assumed to be unity at infinit dilution.

It is evident, if solutions in one solvent are alone considered, that the activity of a substance can be defined as the "effective" concentration which would enable mass-action relations to hold accurately,[2] and that the activity coefficient of a substance at high concentration is a relative measure of its effectiveness in influencing any chemical equilibrium in which it is involved compared with its effectiveness at very small concentrations, where its activity coefficient is taken as unity. Thus, if, as above stated, the concentration of un-ionized TlCl is 15 per cent. less in a saturated solution in the presence of TlSCN than it is in a saturated solution in pure water, the activity coefficient of the un-ionized TlCl must be 15 per cent. larger in the former than in the latter solution, since it is in both cases in equilibrium with the same solid phase. Similarly, if the ion-concentration product, $C_{Tl^+}C_{Cl^-}$, is 5 per cent. larger in the former solution, the product of the activity coefficients of the two ions must be 5 per cent. smaller; and, if the two ions deviate equally from normal activity, the activity coefficient of each is 2.5 per cent. smaller

[1] *Z. physik. Chem.*, 61, 129 (1907); *Proc. Am. Acad.*, 43, 259 (1907).

[2] Thus defined, the term "activity" is substantially identical with the term "active mass," which has been used, often somewhat vaguely, by earlier investigators. A great advantage of Lewis' treatment is that it shows how this quantity is related thermodynamically to other quantities, such as distribution coefficient, electromotive force of concentration cells, osmotic pressure, etc.

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in the TlSCN solution than in the saturated solution in pure water.[1]

We may, therefore, hope, with the aid of the solubility data, not only to study the deviations from the solubility principles, but also to determin in what measure the well-known deviation from the theoretical dilution law is due to abnormal behavior of the ions and in what measure to abnormal behavior of the un-ionized substance. A substance dissolved in water is considered to be normal when its activity (as defined above) is equal to its concentration.

The results of this investigation will be presented in a series of articles. The second part of the present article will consist of a brief discussion of the data already published in regard to solubility effect in cases where a uni-bivalent salt is present as solid phase, the matter being there considered only in its general aspects, but not with reference to the detailed method of treatment described in the preceding pages. In the second and third articles will be presented the results of several new series of solubility determinations made in this laboratory with uni-univalent substances present as the solid phases. Article IV will contain the theoretical discussion of these and some other previously obtained results with uni-univalent salts, along the lines above indicated. In article V, VI and VII the results of new experimental investigations of the solubility of various uni-bivalent salts in the presence of other salts will be described and discussed.

B. Preliminary Note on the Effect of Salts on the Solubility of Uni-bivalent Salts.

It is our purpose in this note to call attention to a certain effect uniformly observed when the solubility of uni-bivalent salts is studied in the presence of another salt having the bivalent ion in common, since the general character of this effect does not seem to have been previously recognized.

In all the cases of moderately soluble uni-bivalent salts (B_2A or A_2B) thus far investigated, it has been found namely, that, though the solubility is reduced in at least rough conformity with the requirements of

[1] In order to avoid misunderstanding with regard to the use of the activity concept, it seems desirable to point out that it may be considered merely a simple method of expressing the results obtained with a given set of assumptions. It assists in comparing the results obtained with different substances, and does not interfere with the adoption of some more concrete explanation of these. Thus, a change in the activity coefficient of a dissolved substance may be due to a "change in the nature of the solvent" or to a "solvent action" produced by the added salt. Such an effect must undoubtedly be taken into account in concentrated solutions (compare Kendall, *Proc. Roy. Soc.*, **85**, 200 (1911)), and it is extremely improbable that it is negligible in solutions as concentrated as 0.1 normal. Or, to take another example, a marked change in the apparent activity coefficient of a bivalent ion (such as $SO^{=}$) might be caused by the conversion of a certain proportion of it into an intermediate ion (such as $AgSO_4^{-}$).

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the solubility-product principle ($C^2_{B^{++}}C_{A^{=}}$ = const., or $C_{B^{++}}C_{A^{-}}{}^2$ = const.) when a salt is added having the *uni*-valent ion (B^+ or A^-) in common, this is by no means the case when a salt is added having the *bi*-valent ion ($A^=$ or B^{++}) in common. In the latter case, the decrease of the solubility caused by the addition of an equivalent quantity of the second salt with a common bivalent ion does not exceed a few per cent. even when the solubility is as small as 0.04 molal, and the addition of a larger quantity causes the solubility to increase. Thus in the case of lead chloride there is a slight initial decrease on the first addition of lead nitrate but on further addition the solubility soon becomes greater than that in pure water. In the case of much more soluble salts, such as barium hydroxide in the presence of barium nitrate and barium nitrate in the presence of barium hydroxide,[1] even a small addition of the second salt causes an increase of the solubility.

These statements are illustrated by the accompanying figure in which the solubilities of lead chloride,[2] thallous oxalate,[3] silver sulfate,[4] and calcium hydroxide[5] are plotted as ordinates and the concentration of the added salts as abscissas.[6] The solubilities are expressed in formula weights per liter, and the concentrations of the added salts in equivalents per liter. In a similar diagram at the end of the second article of this series it is shown that the effect of sodium sulfate on the solubility of thallous sulfate is similar to the effect of lead nitrate on the solubility of lead chloride.

These results show that the solubility-product principle is not even approximately true in the cases when a salt with a common bivalent ion is added, for the ion-concentration-product $C_{B^{++}}C_{A^{-}}{}^2$ or $C_{B^{+}}{}^2C_{A^{--}}$ evidently increases greatly, since the large addition of the bivalent ion is not compensated by any considerable decrease of the uni-valent ion of the salt with which the solution is saturated.

The suggestion has been made in specific instances of this kind that the increase or too small decrease of the solubility is due to the combi-

[1] Parsons and Corson, THIS JOURNAL, 32, 1383 (1910).

[2] Noyes, *Z. physik. Chem.*, 9, 629 (1892). Von Ende, *Z. anorg. Chem.*, 26, 151 (1901).

[3] Abegg and Spencer, *Z. anorg. Chem.*, 46, 406 (1905).

[4] Drucker, *Ibid.*, 28, 362 (1901).

[5] d'Anselme, *Bull. soc. chim.*, [3] 29, 938 (1903). According to Zahorsky, *Z. anorg. Chem.*, 3, 41 (1893), the solubility of calcium hydroxide in an approximately normal calcium chloride solution is practically the same as in water and is increased by further additions of calcium chloride. It therefore seems probable that the initial depressing effect of this salt on the solubility of calcium hydroxide is not very great.

[6] The data for these substances are in general not sufficient to permit of an exact quantitative study, and for this reason the positions of the curves are to be considered only approximate.

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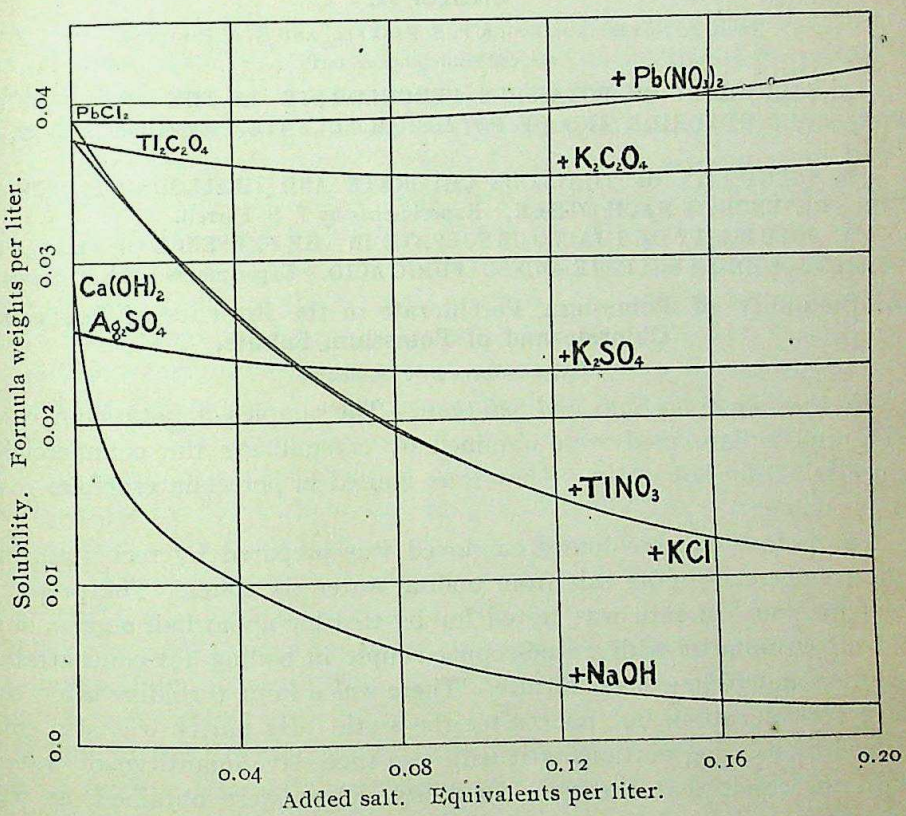
nation of the two salts with the formation of a specific complex cation or anion. We desire to call attention to the fact that the uniformity of the results with so many entirely different salts requires a more general



explanation. Thus it is possible that the effect is due to the presence of the intermediate ion ($ClPb^+$, $AgSO_4^-$, etc.), since this may well be present in corresponding quantities in solutions of all uni-bivalent salts.[1] However this may be, we wish especially to emphasize the view that the effect in question is not specific or exceptional, but is the normal one in the case of salts of this type.

We will not, however, follow the matter further at this point, as Dr. W. D. Harkins has determined, in this laboratory, the solubility of several additional uni-bivalent salts in the presence of various other salts, and will discuss carefully all available data in the seventh article of this series.

[1] This explanation has already been suggested to account for specific results, thus by Von Ende, *Loc. cit.*, in the case of lead chloride, and by Abegg and Spencer, *Loc. cit.*, in the case of thallous oxalate.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 73.]

THE EFFECT OF SALTS ON THE SOLUBILITY OF OTHER SALTS. II.

BY A. A. NOYES, C. R. BOGGS, F. S. FARRELL, AND M. A. STEWART.

Received September 22, 1911.

A. SOLUBILITY OF POTASSIUM PERCHLORATE IN THE PRESENCE OF POTASSIUM CHLORIDE AND OF POTASSIUM SULFATE. Experiments by C. R. Boggs.

B. SOLUBILITY OF THALLOUS CHLORATE AND THALLOUS SULFATE IN THE PRESENCE OF EACH OTHER. Experiments by F. S. Farrell.

C. SOLUBILITY OF THALLOUS SULFATE IN THE PRESENCE OF THALLOUS NITRATE, SODIUM SULFATE AND SULFURIC ACID. Experiments by M. A. Stewart.

A. Solubility of Potassium Perchlorate in the Presence of Potassium Chloride and of Potassium Sulfate.

EXPERIMENTS BY C. R. BOGGS.

Preparation of the Salts and Solutions.—The samples of potassium chloride and sulfate used were obtained by crystallizing the commercially pure salt from hot water. They were ignited in porcelain crucibles over a gas flame.

The potassium perchlorate employed was prepared by recrystallizing the commercially pure salt from boiling water six times. The presence of potassium chlorate was tested for by treating about half a gram of it for fifteen minutes with a zinc-copper couple in boiling-hot concentrated solution and adding silver nitrate. There was a faint turbidity after the fifth crystallization, but none after the sixth. Its purity was also confirmed by rotating portions of it with two successive quantities of water, with the result that the same solubility values were obtained, as will be seen from Table I.

The water used was ordinary distilled water, but its specific conductance did not exceed 5×10^{-6}. Approximately 0.1 and 0.2 normal solutions of potassium chloride and of potassium sulfate were prepared by dissolving the weights of the salts given below in a true liter of water at 25°. An approximately 0.05 normal solution of each salt was prepared by weighing out 251.86 g. of the 0.1 *N* KCl solution, or 252.18 g. of the 0.1 *N* K_2SO_4 solution, and adding in each case 250 g. water. All weights are those in air (uncorrected for air buoyancy). The compositions[1] by weight of these solutions were as follows:

[1] The corresponding concentrations of these solutions expressed in equivalents per liter of solution at 25° were calculated (using 1910 atomic weights) for use in connection with the conductance measurements given below:

	KCl.	K_2SO_4.
Approx. 0.05 *N*	0.04998 *N*	0.0500 *N*
Approx. 0.1 *N*	0.0998 *N*	0.0999 *N*
Approx. 0.2 *N*	0.1991 *N*	0.1995 *N*

To enable these calculations to be made the densities of the 0.2 and 0.1 normal solu-

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	KCl. Grams.	K_2SO_4. Grams.	H_2O. Grams.
Approx. 0.05 *N*	1.8712	2.1872	500.0
Approx. 0.1 *N*	7.456	8.715	996.1
Approx. 0.2 *N*	14.912	17.429	996.1

Method of Determining the Solubility.—The bottles containing the solutions to be saturated were rotated by means of the apparatus previously described[1] for four hours in a thermostat kept within 0.02° or 25°. The temperature was determined with a thermometer that had been compared with a Reichsanstalt standard. These solutions were allowed to settle, while standing in the thermostat, and 100.2 cc. portions were drawn out of each bottle through a cotton filter which had first been washed with a little of the same solution. The portions of the saturated solutions were run into platinum dishes and weighed. Saturation was reached in each case, since the values of the solubility were obtained from experiments in which equilibrium was approached both from above and below 25°, and the results by these two processes check within the error of the determination. The solutions were evaporated to dryness on the steam bath, the residues were heated for fifteen minutes as 200°, then cooled in a desiccator for half an hour, and weighed as quickly as possible. The residues were again heated to 200° and weighed, this process being repeated till the weights were constant within 0.5 milligram.

The weight of water in the portion of solution taken was next determined by difference and the corresponding amount of potassium chloride or potassium sulfate calculated from the composition of the original solution. Finally by subtracting this weight from the total weight of the residue the weight of the potassium perchlorate was determined.[2]

The Solubility Data.—The experimental data are given in Table I.

tions were measured by using a Mohr-Westphal balance, which had been adjusted at 25°, and the corresponding values for the 0.05 normal solutions were determined by extrapolation. The reduction from 25°/25° to 25°/4° was made by multiplying by the factor 0.9971, the density of water at 25°. The values obtained were as follows:

Solution. KCl.	Density referred to water. 25°/25°.	25°/4°.	Solution. K_2SO_4.	Density referred to water. 25°/25°.	25°/4°.
0.05 *N*	(1.0023)	(0.9994)	0.05 *N*	(1.0034)	(1.0005)
0.1 *N*	1.0046	1.0017	0.1 *N*	1.0069	1.0040
0.2 *N*	1.0093	1.0064	0.2 *N*	1.0138	1.0109

[1] *Z. physik. Chem.*, 9, 606 (1892). Ostwald-Luther, *Physiko-Chemische Messungen* (1902), page 281.

[2] This method was tested by dissolving a weighed amount of perchlorate in the 0.1 normal solution of potassium chloride:

$KClO_4$ taken	0.6926 gram	1.2580 grams.
$KClO_4$ found	0.6914 gram	1.2608 grams.

It will be noted that one weight decreased about 0.2 per cent. while the other increased by about the same amount.

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The numbers are the weights in grams contained in 100.2 cc. of the saturated solutions. The third column shows the mean values of the weights of solution taken in each set of experiments; the variation of the separate values from the mean did not exceed 0.1 per cent. The mean values of the total weights of the salts are printed in italics.

TABLE I.—SOLUBILITY DATA FOR POTASSIUM PERCHLORATE.

No. Solvent.	Mean weight of solution.	Total weight of the salts. Equilibrium from Oversatd.	Undersatd.	Weight of water.	Weight of KCl or K_2SO_4.	Weight of $KClO_4$.
1. Water	..	2.0568	2.0560	..	..	..
	..	2.0567	2.0568	..	..	..
	..	*2.0566*		..	..	2.0566
2. KCl solution approx. 0.05*N*	..	..	2.1494	..	..	..
	..	2.1538	2.1490	..	..	..
	101.42	*2.1515*		99.27	0.3715	1.7800
3. KCl solution approx. 0.1 *N*	..	..	2.3025	..	..	..
	..	2.2977	2.3034	..	..	..
	..	2.3044	2.3010	..	..	..
	101.45	*2.3018*		99.15	0.7421	1.5597
4. K_2SO_4 solution approx. 0.05 *N*	..	2.2593	2.2625	..	..	..
	..	2.2587	2.2598	..	..	..
	101.47	*2.2601*		99.21	0.4339	1.8262
5. K_2SO_4 solution approx. 0.1 *N*	..	2.5053	2.5060	..	..	..
	..	2.5075	2.5057	..	..	..
	101.55	*2.5061*		99.04	0.8665	1.6396

The final values of the solubility of the perchlorate and of the concentration of potassium chloride or potassium sulfate in these saturated solutions are given in Table II, in equivalents per liter. The International atomic weights for 1910 were used.

TABLE II.—FINAL VALUES OF THE SOLUBILITY OF POTASSIUM PERCHLORATE AT 25° (EQUIVALENTS PER LITER).

No.	Salt added.	Concentration of salt.	Solubility of $KClO_4$.
1	none	0	0.1481
2	KCl	0.04973	0.1282
3	KCl	0.09933	0.1123
4	K_2SO_4	0.04970	0.1315
5	K_2SO_4	0.09922	0.1181

Discussion of the Solubility Data.—From an examination of Table I, it will be seen that there is no systematic difference between the results obtained by approaching equilibrium from the two opposit directions; also that the divergence of the separate values from the mean does not exceed 0.15 per cent., except in one instance. It may also be mentioned

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that the value (0.1481) of the solubility in pure water here obtained and that (0.1478) derived by interpolation from the results of Noyes and Sammet[1] at 10, 20 and 30° agree within the errors of experiment and interpolation.

It will be observed that potassium sulfate, in correspondence with its smaller ionization, has a somewhat less effect than potassium chloride in reducing the solubility of the perchlorate. The quantitative discussion of the solubility effects will be presented in a later article. The conductance measurements, which are needed for checking these calculations and for determining the ionization values involved, are presented in the following section.

Conductance Measurements.—All conductance measurements were made at 25° by the usual Kohlrausch method. A cylindrical cell with horizontal electrodes was used. The conductance capacity was determined by means of a potassium chloride solution, 0.1 normal at 18°, made by dissolving 3.715 grams potassium chloride (weighed in air) in 500 grams of solution.[2] The specific conductance of this solution at 25° was taken as 0.01289 in accordance with the value found by Kohlrausch and Maltby at 18° (0.01120) and Déguisne's temperature coefficients. From this value (0.01289) the specific conductance at 25° of a potassium chloride solution, 0.1 normal at 25° (using 1910 atomic weights), was calculated to be 0.01290, which agrees perfectly with the value found in this laboratory by Mr. A. C. Melcher.

The following table contains the results of the conductance measurements with the saturated solutions. C denotes the equivalent concentration, and L the specific conductance. The equivalent conductance Λ of the $KClO_4$ solution is also included in the table.

TABLE III.—CONDUCTANCE OF SOLUTIONS SATURATED WITH $KClO_4$.

Exp. No.	C_{KClO_4}.	C_{KCl}.	$C_{K_2SO_4}$.	L.	Λ.
1	0.1481	...	...	0.01650	111.4
2	0.1282	0.04973	...	0.02029	..
3	0.1123	0.09933	...	0.02484	..
4	0.1315	...	0.04970	0.01946*	..
5	0.1181	...	0.09922	0.02263**	..

* Mean of two concordant determinations.

** Mean of two independent determinations which gave 0.02265 and 0.02260.

The conductance at 25° of the approximately 0.1 and 0.2 normal potassium chloride and sulfate solutions was also measured. In Table IV these results are compared with the more recent (unpublished) values obtained by Mr. Melcher, and it is evident that the error in the earlier measurements does not exceed 0.25 per cent.

[1] Noyes and Sammet, *Z. physik. Chem.*, 43, 534 (1903).

[2] Kohlrausch and Holborn, Leitvermögen (1898), page 77.

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TABLE IV.—CONDUCTANCE OF KCl AND K_2SO_4 SOLUTIONS.

Exp. No.	Salt.	C.	L.	Λ (Boggs).	Λ (Melcher).
1.....	KCl	0.0998	0.01291	129.3	129.0
2.....	K_2SO_4	0.0999	0.01096	109.7	109.9
3.....	K_2SO_4	0.1995	0.02028	101.7	101.4

Ionization Values.—In order to calculate the degree of ionization of potassium perchlorate in its saturated solution the value at 25° of Λ_0, the conductance at zero concentration, was derived by interpolation from the values of Noyes and Sammet at 10°, 20° and 30° and found to be 143.0. The degree of ionization (γ) is therefore 111.4/143.0 = 0.779 at the concentration $C = 0.1481$.

In order to check this result Noyes and Sammet's conductance measurements at 20° and 30° were plotted in the familiar $1/\Lambda$, $(C\Lambda)^{n-1}$ diagram and n was assured to be 1.50; the degree of ionization at the concentration 0.1481 was then calculated to be 0.779 at 30° and 0.776 at 20°. Accordingly the exponent $n = 1.50$ was used and the value

$$K = (C\gamma)^n/C(1-\gamma) = 1.194$$

calculated. From this function the percentage ionizations (100γ) at the concentrations 0.1 and 0.2 normal were calculated and are given in Table V.

Table V also contains ionization values for potassium chloride and potassium sulfate derived from Mr. Melcher's conductance data by means of the Λ_0 values, 150.6 and 154.8 respectively.

TABLE V.—IONIZATION VALUES OF KCl, $KClO_4$ AND K_2SO_4 AT 25°.

	KCl.		$KClO_4$ (calc.).		K_2SO_4.	
Equiv. conc.	Percent. ioniz.	Ion-conc.	Percent. ioniz.	Ion-conc.	Per cent. ioniz.	Ion-conc.
0.4	78.9	0.3156	..	..	60.1	0.2404
0.2	82.47	0.1649	75.5	0.1510	65.5	0.1310
0.1	85.65	0.08565	80.8	0.0808	71.0	0.0710
0.05	88.75	0.04437	..	..	76.33	0.03817

B. Solubility of Thallous Chlorate and Thallous Sulfate in the Presence of Each Other.

EXPERIMENTS BY F. S. FARRELL.

In this part are presented the results of experiments on the solubility at 20° of thallous sulfate and thallous chlorate when each salt is present in water alone and when both are present together as solid phases. Conductance measurements with the saturated solutions and with very dilute solutions of these salts are also described.

Preparation of the Salts.—The thallous sulfate was made from metallic thallium by digesting the finely cut metal with fairly strong sulfuric acid (1.65 sp. gr.), diluting the solution and precipitating the salt with alcohol. It was then recrystallized four times from boiling water till the last traces of acid had disappeared.

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The thallous chlorate was made by mixing hot, neutral solutions containing equivalent quantities of barium chlorate and thallous sulfate. The barium sulfate was filtered from the hot solution. The salt which crystallized out on cooling was then purified by four successive crystallizations.

Method of Determining the Solubility.—The solubility determinations were made by rotating from two to three hours 5–6 grams of each of the finely crystallized but not powdered salts with water in oil-sample bottles of about 125 cc. capacity. The thermostat was kept at 20° (± 0.03°), the thermometer used having been compared with two independently standardized ones. In order to insure the attainment of equilibrium, saturation was approached from both the under- and the supersaturated side. Supersaturation was reached by shaking the mixtures at a higher temperature. The contents of the bottle were allowed to settle, and one or two 50 cc. portions were drawn out through a filter consisting of a piece of cotton wool held over the end of the pipet by a piece of rubber tubing.

When only one of the salts was present, the analysis was made by evaporating the portion in a platinum dish on a steam bath, and drying the residue to a constant weight at 150–160° in the case of the sulfate and 130° in the case of the chlorate.

When both sulfate and chlorate were present, two 50 cc. portions of the solution were separately analyzed in the following manner: One portion was evaporated to dryness in a weighed platinum dish and dried at 130° till its weight was constant. The residue was dissolved in 400 cc. water, the solution heated to boiling and an excess of 0.1 normal barium chloride solution added. The precipitated barium sulfate was allowed to settle out on the steam bath, and it was then filtered out, washed, dried, and ignited to a constant weight in a platinum crucible.

The other portion was transferred to a 100 cc. Erlenmeyer flask, the bottom of which was covered with chloride-free metallic zinc. The flask was now placed on the steam bath and enough sulfuric acid (sp. gr. 1.20) added, from time to time, to keep up a moderate evolution of gas. Trial analyses[1] showed that the time necessary for complete reduction is about 8–10 hours, but for security the reduction was continued for at least twelve hours. The zinc was then filtered off and washed,

[1] The results of these trial analyses were as follows:

Expt. No.	Time of reduction in hours.	Wt. of $TlClO_3$ taken.	Wt. of AgCl obtained.	Percent. of Cl in $TlClO_3$. Calc.	Found.
1	4	1.9200	0.9421	12.32	12.13
2	4	1.9343	0.9548	12.32	12.21
3	8–10	1.9220	0.9576	12.32	12.32
4	8–10	1.9380	0.9637	12.32	12.29

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and a slight excess of silver nitrate added to the filtrate. The silver chloride was filtered off, dried at 130°, and weighed in a platinum Gooch crucible.

The Solubility Data.—The following tables contain the data of the solubility experiments. The letters *u* and *s* denote that equilibrium was approached from undersaturation and supersaturation respectively. The International atomic weights for 1910 were employed in all the calculations.

TABLE VI.—SOLUBILITY DATA FOR Tl_2SO_4 AND $TlClO_3$ AT 20°.

Cc. of solution.	Grams of Tl_2SO_4.	Grams of Tl_2SO_4 per liter.	Cc. of solution.	Grams of $TlClO_3$.	Grams of salt per liter.
50.07	2.4341	48.61 *u*	50.01	1.9200	38.39 *u*
50.07	2.4294	48.50 *u*	50.13	1.9343	38.59 *s*
49.97	2.4292	48.61 *s*	50.01	1.9220	38.41 *u*
49.97	2.4263	48.56 *s*	50.13	1.9380	38.67 *s*
49.97	2.4325	48.68 *s*	50.07	1.9220	38.38 *u*
			50.13	1.9330	38.57 *s*
Mean, 48.59; a. d. = 0.05			49.97	1.9219	38.47 *u*
			50.01	1.9332	38.65 *s*
			50.07	1.9266	38.44 *u*
			49 97	1.9312	38.65 *s*
				Mean 38.51 a. d. = 0.10	

TABLE VII.—DATA ON THE SOLUBILITY OF $TlClO_3$ AND Tl_2SO_4 WHEN PRESENT TOGETHER AT 20°.

Expt. No.	Cc. of solution.	Weight of both salts.	Weight of $BaSO_4$.	Cc. of solution.	Weight of AgCl.
1	50.07	3.2477	0.7984	49.97	0.7544
2	50.13	3.2464	0.7997	50.01	0.7504
3	50.13	3.2527	0.7999	50.01	0.7594
4	50.07	3.2380	lost	49.97	0.7594
5	50.13	3.2529	0.8014	50.01	0.7596
6	50.07	3.2498	0.7993	49.97	0.7585
7	50.13	3.2427	0.8009	50.01	0.7566

TABLE VIII.—DATA ON THE SOLUBILITY OF $TlClO_3$ AND Tl_2SO_4 WHEN PRESENT TOGETHER (EXPRESSED IN GRAMS PER LITER).

Expt. No.	Total salt.	Tl_2SO_4 (by anal.).	Tl_2SO_4 (by diff.).	$TlClO_3$ (by anal.).	$TlClO_3$ (by diff.).
1	64.86	34.43	34.59*	30.27*	30.43
2	64.76	34.44	34.67*	30.09*	30.32
3	64.88	34.45	34.43	30.45	30.43
4	64.67*	lost	34.19*	30.48	lost
5	64.89	34.52	34.43	30.46	30.37
6	64.90	34.47	34.36	30.44	30.43
7	64.69	34.51	34.35	30.34	30.18
Mean,	64.83	34.47	34.39	30.43	30.36

* Omitted in calculation of the mean.

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SUMMARY.

	Tl_2SO_4.	$TlClO_3$.
Mean weight (by analysis)	34.47	30.43
Mean weight (by difference)	34.39	30.36
Final weight	34.43	30.40

TABLE IX.—FINAL VALUES OF THE SOLUBILITIES OF THALLOUS CHLORATE AND THALLOUS SULFATE AT 20° (EQUIVALENTS PER LITER).

$TlClO_3$	0.1340	0.0	0.1058
Tl_2SO_4	0.0	0.1928	0.1366

The summary of the results in Table IX shows to what extent the solubility of each of the salts in water alone is reduced by the presence of the other salt. An examination of the experimental data indicates that the results are probably accurate to about 0.1 per cent. This conclusion is confirmed by the fact that an entirely independent determination of the solubility of thallous sulfate in this laboratory by Dr. H. T. Kalmus[1] gave the value 0.09642 mol. per liter at 20°, which is identical with the present value.

Conductance Measurements.—The conductance measurements were made in duplicate at 20° by the usual bridge method, employing a U-shaped resistance cell of 50 cc. capacity for the saturated solutions and a cylindrical cell for the dilute ones. The saturated solutions and also 0.001 normal solutions of the separate salts were measured, and all these solutions were prepared by dissolving weighed amounts of the salt in calibrated flasks. The results of the measurements are given in Table X.

TABLE X.—CONDUCTANCE OF SOLUTIONS OF THALLOUS SULFATE AND THALLOUS CHLORATE AT 20°.

Concs. Tl_2SO_4.	(Milli-equiv.). $TlClO_3$.	Specific cond. × 10^4. Separate values		Mean.	Equiv. cond.
192.8	0.0	149.5	149.3	14.94	77.5
1.001	0.0	1.330	1.332	1.331	133.0
0.0	134.0	135.5	135.3	135.4	101.0
0.0	1.001	1.241	1.242	1.242	124.1
136.6	105.8	200.7			

A check on these results is furnished in the case of thallous sulfate by a more recent, extended series of measurements at 18° and 25° made by Mr. F. L. Hunt[2] in this laboratory. From these results, by assuming a slightly smaller degree of ionization at 20° than at 18°, the values of the equivalent conductance at 0.001 and 0.1928 normal were calculated to be 133.0 and 77.43 respectively, in good agreement with the present results. Further excellent checks are furnished by independent de-

[1] *Physics Theses M. I. T.* (1904).
[2] THIS JOURNAL, **33**, 802 (1911).

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terminations of the conductance of a saturated solution at 20° by H. T. Kalmus[1] and by W. H. Whitcomb[2] in this laboratory; after correcting to 1910 atomic weights the values are 77.6 and 77.44 respectively.

Ionization Values.—The ionization values for thallous sulfate at 20°, given in Table XI, were calculated from the data of Hunt at 18° and 25° by extrapolating to concentrations higher than 0.2 normal by means of a $1/\Lambda$, $(C\Lambda)^{0.5}$ plot. These values are almost identical with those obtained at an earlier date by means of a similar plot based on the two available measurements at 20° (Table X). The values of Λ_0 were assumed to be 134.4, 140.4 and 156.2 at 18°, 20° and 25° respectively.

Ionization values for thallous sulfate (Table XI) were also obtained by means of a $1/\Lambda$, $(C\Lambda)^{0.5}$ plot based on the above conductance data at 20° (assuming Λ_0 = 126.2 at 20°), but there is at present no means of checking the calculations as in the case of thallous sulfate. It is interesting to note that thallous chlorate is slightly less ionized than potassium chlorate or potassium nitrate, butis more highly ionized than thallous nitrate.

TABLE XI.—IONIZATION VALUES OF Tl_2SO_4 AND $TlClO_3$ AT 20°.

Equiv. conc.	Percentage ionization.	Ion conc.	Equiv. conc.	Percentage ionization.	Ion conc.
0.20	54.8	0.1096	0.1340	80.1	0.1073
0.25	52.5	0.1313	0.1844	77.6	0.1431
0.30	50.7	0.1521	0.2421	75.4	0.1826
0.35	49.2	0.1720			
0.40	48.0	0.1920			

C. Solubility of Thallous Sulfate in the Presence of Thallous Nitrate Sodium Sulfate and Sulfuric Acid.

EXPERIMENTS BY M. A. STEWART.

In this part experiments are described on the solubility of thallous sulfate at 25° in water and in the following solutions: 0.1 formal $TlNO_3$, 0.2 and 0.5 formal Na_2SO_4, 0.1 formal $NaHSO_4$, and 0.1 and 0.5 formal H_2SO_4. The effect of the last two substances was investigated in connection with the research on the ionization relations of sulfuric acid,[3] and the discussion of the results will be postponed until after the solubility relations of other uni-bivalent salts have been examined.

The conductivity of the saturated solutions was also measured; and the density of the solutions before and after saturation was determined in order to obtain the change in concentration of the original solute due to the increase in volume attending the saturation with thallous sulfate.

Preparation of the Substances and Solutions.—The thallous sulfate was prepared substantially as described in the previous article by F. S. Farrell.

[1] *M. I. T. Physics Theses* (1904).
[2] *M. I. T. Chemical Theses* (1906).
[3] THIS JOURNAL, 32, 1133 (1910).

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Two separate preparations designated below, Sample I and Sample II, were used.

The water used in this investigation was conductivity water with a specific conductance between 1 and 2×10^{-6}. All concentrations are expressed in formula weights per liter referred to the International atomic weights for 1907 but are only 0.04 to 0.06 per cent. smaller than if 1911 atomic weights had been used.

The 0.2 formal sulfate solution was prepared by weighing out the ignited salt and making it up to the proper volume at 25°. The 0.05 formal solution was made from this one by dilution. The sodium sulfate was purified by heating a solution saturated at 33° to boiling and filtering out the precipitate, which was washed with a little hot water and heated for two hours at a dull red heat. Tests made upon it showed no trace of potassium or chloride.

The 0.1 *F* $NaHSO_4$ solution was one of the solutions used in the transference measurements.[1]

The sulfuric acid solutions were made by diluting a 0.2 formal acid, which had been prepared from Baker and Adamson's chemically pure sulfuric acid, and which had been standardized by titration with well ignited sodium carbonate.

The thallium nitrate was prepared by dissolving the metal, cut up into small pieces, in hot nitric acid (1.10 sp. gr.). On cooling, the greater part of the thallous nitrate crystallized out, and the remainder was precipitated by the addition of alcohol. The salt was filtered off, washed with alcohol, recrystallized twice from hot water, washed once with cold water and dried for three hours at 120–140°. The thallium nitrate solution was prepared by making up a weighed amount of thallium nitrate to the proper volume at 25°. The thallous content of the solution was also determined by two titrations with potassium permanganate by the method described below, the results obtained being 0.10013 and 0.10009, showing the absence of thallic salt.

Description of the Experiments.—The solutions were saturated with thallous sulfate by placing an excess of it with the desired solution in tightly stoppered bottles, and rotating them for four to twenty hours in a thermostat at 25° ± 0.02°. In some cases saturation was approached from a higher and in other cases from a lower temperature.

The amount of thallous sulfate dissolved was determined as follows: A sample from the bottle was drawn into a clean, dry pipet (of 14.754 cc. capacity) through a cotton plug placed in a cap on the end of the pipet, and the liquid was made up to 500 cc.; 100 cc. of this solution were diluted to about 500 cc., 40 cc. of HCl (1.20) added, and the mixture was

[1] THIS JOURNAL, 32, 1151 (1910).

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titrated with dilute potassium permanganate solution, whereby the thallous is converted to the thallic salt. The permanganate solution was standardized against thallous sulfate that had been heated at 230° for four hours.

This titration requires certain precautions. After many trials the proper conditions were found to be as follows:

1. The concentration of hydrochloric acid[1] in the solution to be titrated must be that produced by the addition of between 38 cc. and 42 cc. of acid of specific gravity 1.20 to 500 cc. of the solution. Much less than 38 cc. is likely to allow a brown precipitate of hydrated manganese oxides to separate and therefore mask the end point. More than 42 cc. causes the end point to fade away very rapidly. 2. The solution must be diluted enough to insure the non-precipitation of thallous chloride on addition of the hydrochloric acid. 3. The standard potassium permanganate solution used, must be dilute, containing not more than 2.0 g. $KMnO_4$ per liter, best 1.0 to 1.5 g. 4. The permanganate solution must be run in very slowly (drop by drop) and the solution must be constantly and thoroughly stirred; for, otherwise, the hydrochloric acid will react with the permanganate, liberating chlorine, before it is all used up by the thallium. With these precautions, the method gives concordant results.

The conductance of the solutions was measured in a specially made U-shaped cell 8 cc. in volume and of suitable resistance. The conductance capacity was determined with a potassium chloride solution (0.02 normal at 25°), the specific conductance of which was assumed to be 0.002770.[2]

The Experimental Data.—The experimental data relating to the saturated solutions are presented in Table XII and the results summarized in Table XIII. The solubilities at 25° are expressed in formula weights Tl_2SO_4 per liter, and the symbols S_I and S_{II} refer to Sample I and Sample II respectively. In almost every case two or three separate portions of the same solution were titrated, and the separate results differed from the mean by less than 0.1 per cent. Only the mean value is given in the table. When the letter *s* is attached to the number, it indicates that equilibrium was approached from supersaturation. C_o and C denote the formal concentrations of the salt solution before and after saturation with thallous sulfate; D_o and D denote the corresponding densities. *L* is the specific conductance of the saturated solution.

[1] Sulfuric acid can not be used, because, even a large amount of it will not prevent the precipitation of the brown precipitate.

[2] This value is a mean between that calculated from the results of Kohlrausch and Maltby at 18° and the temperature coefficient of Déguisne and corrected for the expansion of the solution between 18° and 25° (0.002767), and a recent result obtained by Mr. A. C. Melcher, of this laboratory (0.002773).

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TABLE XII.—EXPERIMENTAL DATA.

S_I.	S_{II}.	$L \times 1000$.	D.	C.
		Water		
0.1084*	0.1084			
0.1083*	....			
0.1084*s	0.1081 s			
0.1085*s	0.1085*s			
(0.1081*)	(0.1081*)			
Mean, 0.1083				
	Na_2SO_4 soln.:	$C_0 = 0.2000$;	$D_0 = 1.0223$.	
0.1174*	0.1174*	42.08	1.0754	
0.1173*	....	42.09	1.0754	
0.1172*s	0.1173†s	42.15	1.0755	
0.1173*s	....	42.13	..	
Mean, 0.1173		42.11	1.0754	0.1988
	Na_2SO_4 soln.:	$C_0 = 0.04995$;	$D_0 = 1.0035$.	
0.1080*	0.1080*	24.20	1.0531	
0.1081*	....	24.21	1.0531	
0.1081*s	....	24.23	1.0531	
0.1080*s	....	..	1.0531	
Mean, 0.1080		24.21	1.0531	0.04971
	$NaHSO_4$ soln.:	$C_0 = 0.1015$;	$D_0 = 1.0066$.	
0.1161*	0.1161	39.67	1.0594	
0.1161	0.1161	39.66	..	
0.1162*s	0.1162	39.68	1.0597	
0.1161*s	0.1161 s	..	1.0597	
Mean, 0.1161		39.67	1.0596	0.10096
	H_2SO_4 soln.:	$C_0 = 0.09933$;	$D_0 = 1.0036$.	
0.1250*	0.1249*	53.52	..	
0.1249*	....	53.52	1.0604	
0.1249*s	....	53.52	1.0604	
0.1250*s	....	53.52	1.0604	
Mean, 0.1249		53.52	1.0604	0.09872
	H_2SO_4 soln.:	$C_0 = 0.04967$;	$D_0 = 1.0005$.	
0.1172†	0.1172*	35.27	1.0540	
0.1172*	0.1172	35.27	1.0540	
Mean, 0.1172		35.27	1.0504	0.04939

* Mean of two titrations of same solution.
† Mean of three titrations of same solution.

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TABLE XII (*continued*).

$TlNO_3$ soln.:[1] $C_0 = 0.1000$; $D_0 = 1.0917$.

S_I.	S_{II}.	$L \times 1000$.	D.	C.
0.08365*	0.08363*	23.73	..	
0.08364	0.08362*	23.73	1.0581	
0.08367*s	....	..	1.0582	
0.08368*s	....	23.73	1.0582	
Mean, 0.08365		23.73	1.0582	0.09964

* Mean of two titrations of same solution.

TABLE XIII.—SUMMARY OF SOLUBILITY AND CONDUCTANCE DATA.

Solution.	$1000L$.	Conc. Tl_2SO_4.
Water	..	0.1083
0.0996 F $TlNO_3$	23.73	0.08365
0.0497 F Na_2SO_4	24.21	0.1080
0.1988 F Na_2SO_4	42.11	0.1173
0.1010 F $NaHSO_4$	39.67	0.1161
0.0494 F H_2SO_4	35.27	0.1172
0.0987 F H_2SO_4	53.52	0.1249

The results (except in two cases) are presented in the order in which the measurements were made. The exceptions are the measurements of the solubility of each sample of thallous sulfate in pure water from undersaturation, which were made after all the other determinations had been completed. Since these two concordant values (0.1081) are 0.3 percent less than the mean solubility obtained in the initial measurements (0.1084), it is impossible to claim an absolute accuracy of better than 0.2 or 0.3 per cent. for the final results. The separate determinations in each series are, however, remarkably concordant, and it seems probable that the relative accuracy of the solubilities in the first three series (in water and in sodium sulfate solutions) is about 0.1 per cent.

An examination of the results (Table XIII) shows that the solubility of thallous sulfate is greatly lowered by the presence of thallous nitrate, a salt with a common univalent ion, which is in qualitative agreement with the principle of the constancy of the ionic solubility product. On the other hand, the addition of sodium sulfate, a salt with a common bivalent ion, does not produce the expected lowering. The solubility is reduced only 0.3 per cent. in the 0.1 normal sodium sulfate solution and is actually increased in the more concentrated solution. That the solubilities of other uni-bivalent salts are affected in a similar manner by the addition of salts with common bivalent ions has already been pointed out in Part B of the first article.

[1] Measurements of the conductance of this 0.1 F $TlNO_3$ solution gave the results: L_{25} = 0.01163, 0.01165, 0.01163, 0.01165; mean, 0.01164.

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Summary.

The solubility data contained in this article have been summarized in Tables II, IX and XIII, and are presented graphically in the accompanying figure, in which solubilities are plotted as formula weights per

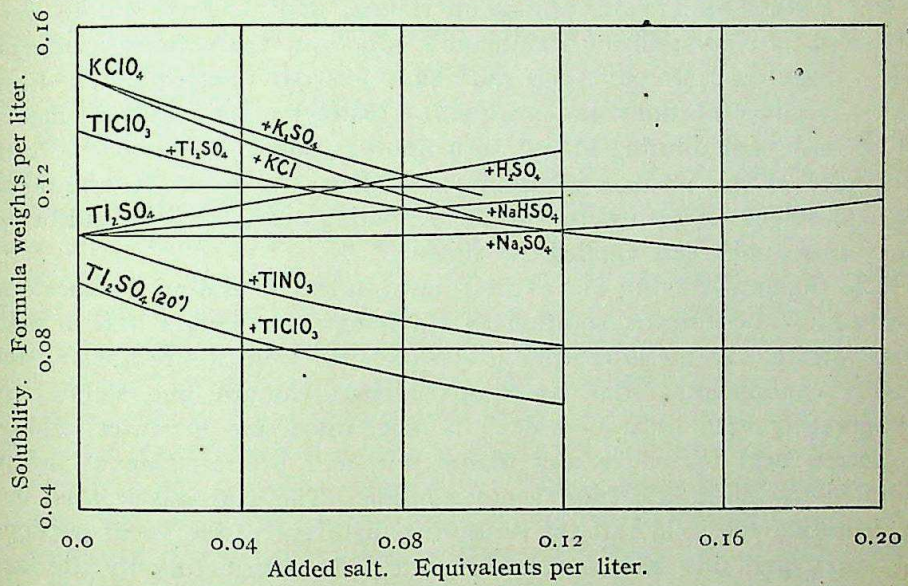

Fig. 1.

liter and the concentrations of the added salts as equivalents per liter. The article also contains the results of some conductance measurements for a number of salts, from which the corresponding ionization values have been calculated. The quantitative discussion of the results is reserved for a later article.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 74.]

THE EFFECT OF SALTS ON THE SOLUBILITY OF OTHER SALTS. III. SOLUBILITY OF THALLOUS CHLORIDE IN SOLUTIONS OF POTASSIUM NITRATE, POTASSIUM SULFATE, AND THALLOUS SULFATE AT 25°.

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This investigation was undertaken to determin the effect on the solubility of thallous chloride of the presence of thallous sulfate, a unibivalent salt with a common ion, and of potassium nitrate and potassium sulfate, salts without a common ion. These experiments supplement those of Noyes[1] on the solubility of thallous chloride in the presence of

[1] A. A. Noyes, *Z. physik. Chem.*, 9, 603 (1892).

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thallous nitrate, thallous chlorate, and a large number of chlorides and thus render possible the examination of the effect on the solubility of thallous chloride of typical uni-univalent and uni-bivalent salts both with and without a common ion.

The potassium nitrate, potassium sulfate, and thallous sulfate were prepared by recrystallizing Kahlbaum's salts from conductivity water and were dried at 120–150°, 260–280° and 300–350° respectively. Each of the various solutions was prepared by dissolving the required amount of the salt and diluting at 25° to a known volume. The specific conductance of the water was usually less than 1×10^{-6}. International atomic weights of 1910 were used in calculating concentrations and buoyancy corrections were applied throughout.

The thallous chloride was at first precipitated by adding hydrochloric acid to hot concentrated solutions of Kahlbaum's thallous sulfate or thallous nitrate. In the later work it was prepared from the residues of the earlier experiments (after removing silver as chloride and sulfide) by evaporating with sulfuric acid to fuming, dissolving in water, adding sulfurous acid to reduce any thallic salt, and precipitating as before with hydrochloric acid from a hot solution. The acid was washed out by rotating the solid salt for some time with successive small portions of water, and this treatment was shown to be satisfactory by the fact that the concentration and conductance of the saturated solution was the same as in the case of a sample of thallous chloride which had been recrystallized twice from conductivity water. After the experiments with potassium nitrate and with potassium sulfate these substances were washed out by the same treatment, and the saturated aqueous solutions were found to have the same conductance and concentration as before.

The thallous chloride was not dried and was kept in the dark. When first prepared it was pure white, but turned pink if heated at 110°, and the wet salt also became pink and finally purple when exposed to the light. In nearly all the experiments the bottles were covered with black cloth to guard against this action of the light, but some special experiments showed that the conductance and concentration of saturated solutions were exactly the same for the purple and white salts.

In each solubility determination 10 to 20 grams thallous chloride were rotated for at least 12 hours at 25° in a 250 cc. "Resistenz" glass bottle nearly filled with conductivity water or a salt solution of known concentration. The bottles were rotated end over end in order to mix the heavy salt with the solution. The stoppers were paraffined and protected by rubber tubing in the usual way. Equilibrium was approached from undersaturation and supersaturation, the latter state being reached by shaking the bottles in hot water at 50° or 60°. The measurements with each salt were made successively from the dilute to the concentrated

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solutions. Before each determination with a given salt solution the thallous chloride was rotated for 3 or 4 hours with about 150 cc. of the salt solution; this was poured off, and the bottle filled with the same solution.

A portion of each saturated solution was first forced directly into a conductance cell of the pipet form and its conductance measured at 25° in the usual way.[1] The density at 25° was then determined with this same solution or sometimes with a fresh portion of the solution in an Ostwald pycnometer[2] of about 20 cc. capacity. The conductances of the salt solutions used in these experiments and of some dilute thallous chloride solutions were also measured and are compared with existing data in Tables III and IV below.

After the conductance had been measured the remainder of each saturated solution (about 200 cc.) was forced through a small asbestos filter into a weighed glass-stoppered flask, weighed, washed into a beaker, and analyzed for chloride by adding a few drops of nitric acid and silver nitrate solution. A nearly equivalent amount of 0.1 normal silver nitrate was added slowly, with vigorous stirring, to the cold solution in the dark, the mixture was allowed to stand about twenty hours in the dark and a 20 per cent. excess of silver nitrate added. After standing over night the precipitate was collected in a Gooch crucible, washed with about 150 cc. water, heated at 100° for an hour and then at 150° for 4 to 12 hours, cooled in a desiccator for one hour and weighed, and finally heated again at 150° and again weighed.

Solubility Data.—The results of the final measurements of the solubility and conductance of saturated thallous chloride solutions are given in Table I. The concentrations in equivalents per liter were calculated

TABLE I.—SOLUBILITY AND CONDUCTANCE OF SATURATED THALLOUS CHLORIDE SOLUTIONS AT 25°.

No.	Conc. × 10^3. Under.	Conc. × 10^3. Super.	Spec. cond. × 10^3.	Equiv. cond. Λ.
1	16.09	.	2.180	135.5
2	.	16.07	2.176	135.4
3	16.07	.	2.176	135.4
4	.	16.05	2.180	135.8
5	16.07	.	2.175	135.4
6	16.07	.	2.175	135.4
7	.	16.04	2.179	135.9
8	16.07	.	2.175	135.4
9	.	16.09	2.175	135.2
10	16.09	.	2.178	135.3
11	.	.	2.175	.
Mean values,	16.07		2.176	135.4

[1] THIS JOURNAL, 33, 796 (1911).
[2] Ostwald-Luther, *Physico-chemische Messungen*, 142 (1902).

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from the experimental data by means of the absolute density $d25°/4° = 0.9994$ (Table II). The first four measurements were made before the experiments with potassium nitrate, the next three before those with potassium sulfate, and the last four before those with thallous sulfate. The results in the seventh experiment were rejected in calculating the mean values. A number of preliminary experiments which are not included in the table gave the same mean value for the concentration and a 0.1 per cent. higher value for the equivalent conductance. The latter value was probably due to the presence of a trace of acid and was rejected.

The final value for the solubility at 25°, 0.01607 mol. per liter, is only 0.13 per cent. lower than an early result of Noyes[1] but differs by 1.4 per cent. from a recent result of Hill,[2] 0.01629. The latter value, however, is based on a volumetric method of analysis and no record of test analyses at the time of the determination is given.

The results of the solubility determinations in the presence of potassium nitrate, potassium sulfate and thallous sulfate are given in Table II. The initial concentration (milliequivalents per liter) and the ab-

TABLE II.—SOLUBILITY OF THALLOUS CHLORIDE IN THE SALT SOLUTIONS.

Salt solution.			Soly. of TlCl × 10³.			Mean		
Salt.	Equiv. conc. × 10³.	$d25°/4°$.	Under.	Super.	Mean.	spec. cond. × 10³.	$d25°/4°$.	Conc. of salt × 10³.
None	...	..	...	...	16.07	2.176	0.9994	..
KNO_3	20.01	0.9973	17.15 17.15	17.17 17.16	17.16	4.807	1.0009	20.00
	50.00	0.9992	18.27 18.25	18.24 18.29	18.26	8.466	1.0028	49.97
	100.05	1.0023	19.62 19.58	19.62 ...	19.61	14.18	1.0063	99.98
	300.2	1.0145	23.13	23.14	23.13	34.62	1.0194	300.0
	1000.5	1.0568	30.76	30.68	30.72	..	1.0632	999.6
K_2SO_4	19.97	0.9975	17.80 17.76	17.83 17.77	17.79	4.644	1.0012	19.96
	50.00	0.9995	19.45 19.39	19.41 19.44	19.42	7.962	1.0037	49.96
	100.0	1.0030	21.36 21.35	21.41 21.35	21.37	13.02	1.0074	99.89
	300.0	1.0167	26.00	25.99	26.00	..	1.0221	299.66
	1000.0	1.0628	34.16 33.86	34.11 34.22	34.16	..	1.0698	998.6
Tl_2SO_4	20.00	1.0007	10.33 10.34	10.35 10.33	10.34	3.620	1.0028	19.99
	50.00	1.0076	6.764 6.777	6.781 6.764	6.772	6.052	1.0090	49.99
	100.0	1.0191	4.673 4.683	4.681 4.678	4.679	10.01	1.0200	99.97

[1] *Z. physik. Chem.*, 9, 609 (1892).
[2] THIS JOURNAL, 32, 1189 (1910).

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solute density ($d25°/4°$) of the salt solutions used are given in the second and third columns of the table, and the concentration of the salt in the saturated solution (after correcting for the slight increase of volume on dissolving thallous chloride) is given in the last column. The solubilities (in millimoles per liter) in columns four and five were derived from the analytical results by means of the densities (column eight). The mean solubilities are given in column six and the specific conductance of the saturated solutions in column seven.

Conductance and Ionization Data.—The results of the conductance measurements at 25° for the potassium nitrate, potassium sulfate, and thallous sulfate solutions were reduced when necessary to round concentrations, and are presented in the following table. The values for the 0.3 normal solutions are less accurate than the results in more dilute solutions. Λ is the equivalent conductance and $C \times 10^3$ the concentration in milliequivalents per liter. These results and those of other investigators[1] (third column) were plotted in $1/\Lambda$ $(C\Lambda)^{n-1}$ diagrams in the usual way, and values were finally chosen for each salt (fourth

TABLE III.—CONDUCTANCE AND IONIZATION DATA AT 25°.

$C \times 10^3$.	Values of Λ. B. & W.	J., M., or H.	Λ_{final}.	100γ.	$\Sigma C_i \times 10^3$.	$K=\frac{(C\gamma)^{1.50}}{C(1-\gamma)}$.	$k=\frac{(C\gamma)(\gamma)}{(1-\gamma)}$.
(KNO_3)							
0.0	..	..	(145.4)	100.0	..	..	..
12.5	..	134.9	134.9	92.8	11.60	1.390	0.1495
20.0	132.5	(132.5)	132.5	91.1	18.24	1.400	0.1866
50.0	126.1	126.3	126.3	86.85	43.43	1.378	0.2870
100.0	120.3	120.3	120.3	82.7	82.7	1.375	0.3950
200.0	113.5[2]	..	113.4	78.0	156.0	1.400	0.553
300.0	108.3	..	108.6	74.7	224.1	1.400	0.656
($^1/_2K_2SO_4$)							
0.0	..	..	(154.8)	100.0	..	..	..
20.0	127.9	128.1	127.9	82.6	16.53	..	0.0784
50.0	117.95	118.15	117.95	76.2	38.10	..	0.1220
100.0	109.8	109.9	109.8	70.9	70.9	..	0.1727
200.0	(101.4)	101.4	101.4	65.5	131.0	..	0.2488
300.0	96.15	..	96.15	62.1	186.4	..	0.3055
($^1/_2Tl_2SO_4$)							
0.0	..	..	(156.2)	100.0	..	..	..
10.0	130.0	130.0	130.0	83.2	8.32	0.4517	0.0412
20.0	120.95	120.9	120.95	77.45	15.49	0.4275	0.0532
50.0	107.1	107.1	107.1	68.54	34.27	0.4033	0.0746
100.0	95.95	96.0	95.95	61.42	61.42	0.3946	0.0978
200.0	..	85.0	85.0	54.4	108.8	0.3935	0.1298
(300.0)	..	..	..	(50.3)	(150.9)	0.3931	0.1527
(400.0)	..	..	..	(47.4)	(189.6)	0.3924	0.1708

[1] Potassium nitrate, Noyes and Johnston, THIS JOURNAL, 31, 979 (1909). Potassium sulfate, preliminary values obtained by Mr. A. C. Melcher, of this laboratory. Thallous sulfate, Hunt, THIS JOURNAL, 33, 802 (1911).

[2] This value of Λ for 0.2 N KNO_3 was measured by Dr. W. D. Harkins.

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column) which were concordant at the different concentrations. From the latter the values of the percentage ionization 100 γ were calculated (fifth column). The corresponding ion concentrations (in milliequivalents), 1000 ΣC_i = 1000 $C\gamma$, are given in the sixth column. Data obtained by interpolation or extrapolation are enclosed in parentheses in Table III to VI. Values of $K = (C\gamma)^n/C(1-\gamma)$ and of $k = (C\gamma)(\gamma)/(1-\gamma)$, which will be used in the later calculations, are also given in the last columns of these tables.

The experimental results for thallous sulfate and potassium agree almost exactly with those of Hunt and of Noyes and Johnston respectively, while the results for potassium sulfate are only 0.1 to 0.2 per cent. less than Melcher's preliminary values.

The data for thallous chloride are given in Table IV. The dilute solutions were prepared by diluting known weights of saturated solutions (specific conductance = 0.002176) to known volumes. The results are shown to be concordant with those of Kohlrausch and Steinwehr at 18°[1] by the comparison of the ionization values at 18° (Λ_0 = 131.4) with those at 25° (columns three and four).[2] The values of the ion concentration ($\Sigma C_i = C\gamma$) are given in the fifth column. These results were shown to obey the law $(\Sigma C\gamma)^{1.6}/C(1-\gamma) = K$, and the calculated values of K are given in the second last column. Ionization values at higher concentrations were calculated by means of this relationship and are included in the table.

TABLE IV.—CONDUCTANCE AND IONIZATION OF TlCl AT 25°.

1000C.	Λmeasured.	100γ(18°).	100γ(25°).	1000(ΣC_i).	$K = \frac{(C\gamma)^{1.6}}{C(1-\gamma)}$.	$k = \frac{(\Sigma C_i)(\gamma)}{(1-\gamma)}$.
0.0	(152.0)	..	100.0	..	..	..
5.07	143.1	94.1	94.1	4.78	0.649	..
6.04	142.25	93.5	93.6	5.64	0.644	..
10.00	139.0	91.5	91.5	9.14	0.641	..
11.08	138.35	91.02	91.0	10.08	0.642	0.102
16.07	135.4	89.1	89.1	14.32	0.640	0.117
(40.0)	..	..	(83.1)	(33.24)	0.636	0.1637
(60.0)	..	..	(79.8)	(47.88)	0.637	0.1891
(80.0)	..	..	(77.2)	(61.76)	0.636	0.2090
(100.0)	..	..	(75.1)	(75.1)	0.638	0.2264
(139.7)	..	..	(71.7)	(100.2)	0.637	0.2540
(200.0)	..	..	(67.8)	(135.6)	0.635	0.2847
(300.0)	..	..	(63.4)	(190.2)	0.637	0.3290
(400.0)	..	..	(60.0)	(240.0)	0.637	0.360

[1] *Landolt-Börnstein-Meyerhoffer, Tabellen* 744 (1905).

[2] Hunt's value of the conductance of the thallium ion at 25°, 76.0 derived from thallous sulfate measurements, has been raised to 76.2 since otherwise the ionization of thallous chloride would have been found to increase with increasing temperature. The ionization values for thallous sulfate given in Table III are therefore somewhat less than those given by Hunt.

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A comparison of the ionization values of thallous chloride with those of other salts (see for example Table I of the following article) shows that this salt is much less ionized than nearly all other uni-univalent salts. Since in the case of salts of a given type the ones least ionized have the largest values of the exponent n, there does not seem to be any reason for choosing a lower value than $n = 1.60$. In order, however, to determin to what extent the results of the extrapolation were influenced by the value assumed for the exponent, some calculations were made for $n = 1.55$, which was regarded as the lowest possible exponent at 0.1 normal concentration. At this concentration γ was found to be 0.766 instead of 0.751, as given in the table, and this difference is not large when the range of the extrapolation is considered.

Ionization values at 25° for use in later calculations were also desired for a number of salts. The values for KCl (Table V) are based on the preliminary conductance results of Mr. A. C. Melcher, of this laboratory, but the values of Λ were reduced by about 0.1 per cent. in two instances as a result of the comparison of the ionization values with those derived from the measurements of Kohlrausch and Maltby at 18°. The ionization values for thallous nitrate (Table VI) were derived from the conductance measurements of Kohlrausch and Steinwehr at 18°. The assumption that the ionization of thallous nitrate is the same at 18° and 25° is supported by a conductance measurement for 0.1 normal $TlNO_3$

TABLE V.—IONIZATION OF KCl AT 25°.

Conc. × 10^3.	$\Lambda_{25°}$. Melcher.	Λused.	100 γ.	$(C\gamma) \times 10^3$.	$K=\frac{(C\gamma)^{1.40}}{C(1-\gamma)}$.	$k=\frac{(C\gamma)(\gamma)}{(1-\gamma)}$.
0	..	(150.6)	100	..	..	..
10	141.4	141.4	93.9	9.39	2.380	0.1445
20	138.65	138.55	92.0	18.40	2.325	0.2117
50	133.65	133.6	88.7	44.35	2.258	0.3480
100	129.0	129.0	85.65	85.65	2.234	0.512
(146)	..	(126.4)	(83.9)	(122.6)	2.263	0.639
200	124.2	124.2	82.47	164.9	2.285	0.776
(300)	..	..	(80.3)	(240.9)	2.309	0.982

TABLE VI.—IONIZATION OF $TlNO_3$ AT 18° AND 25°.

Conc. × 10^3.	$\Lambda_{18°}$.	100 γ.	$(C\gamma) \times 10^3$.	$K=\frac{(C\gamma)^{1.55}}{C(1-\gamma)}$.	$k=\frac{(C\gamma)(\gamma)}{(1-\gamma)}$.
0	(127.7)	..	..	..	..
10	118.38	92.7	9.27	0.967	0.1176
(28.55)	..	(88.0)	(25.12)	0.965	0.1843
50	107.93	84.52	42.25	0.958	0.2307
(67.1)	..	(82.4)	(55.30)	0.954	0.2590
100	101.91	79.24	79.24	0.947	0.3026
(166.0)	..	(74.7)	(124.0)	0.937	0.366
(220.0)	..	(71.9)	(158.2)	0.928	0.404
(300.0)	..	(68.7)	(206.1)	0.921	0.452

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made by Stewart[1] $\Lambda_{25°} = 116.4$. since the corresponding degree of ionization, $116.4/146.8 = 0.793$, is practically the same as that given in the table, 0.7924.

Discussion of the Solubility Results with Thallous Chloride in the Presence of Other Salts.—The solubility values of thallous chloride in the presence of thallous sulfate, potassium nitrate, and potassium sulfate (Table II) are summarized in the last three columns of Table VII. The earlier results of A. A. Noyes[2] are also presented in this table, but the original numbers have been diminished by 0.3 per cent., since, as pointed out above, the corresponding solubility of thallous chloride exceeds our present value by this amount. The numbers in the third column headed KCl are mean values from the three sets of experiments in which the added salts were potassium, sodium, and ammonium chlorides; and no regular deviations from salt to salt were observed. Similarly the numbers in the fourth column are mean values from experiments with the chlorides of barium, calcium, magnesium, manganese, zinc and copper as in this case also the deviations of the values of the separate salts from the mean values are irregular. An examination of the original data shows, however, that the error in some of the individual results is over 1 per cent. The concentrations are all in milliequivalents per liter.

TABLE VII.—SOLUBILITY OF THALLOUS CHLORIDE IN THE PRESENCE OF OTHER SALTS.

Conc. of added salt.	HCl.	KCl.	$BaCl_2$.	$TlNO_3$.	Tl_2SO_4.	KNO_3.	K_2SO_4.
10	16.07	16.07	16.07	16.07	16.07	16.07	16.07
20	.	.	.	.	10.34	17.16	17.79
25	8.66	8.69	8.98	8.80	.	.	.
50	5.83	5.90	6.18	6.24	6.77	18.26	19.42
100	3.83	3.96	4.16	4.22	4.68	19.61	21.37
200	2.53	2.68	2.82	.	.	.	.
300	.	.	.	.	.	23.13	26.00
1000	.	.	.	.	.	30.72	34.16

These results are presented graphically in the accompanying diagram, but the HCl and $TlNO_3$ curves have not been drawn since they would lie close to the KCl and $BaCl_2$ curves respectively.

The solubility of thallous chloride is seen to increase in the presence of potassium nitrate and of potassium sulfate, the salts without a common ion. This was to be expected on account of the formation of un-ionized thallous nitrate and thallous sulfate by metathesis. The greater increase of solubility in the potassium sulfate solutions corresponds, moreover, to the fact that thallous sulfate is less ionized than thallous nitrate (Table III and VI).

The great decrease in the solubility of thallous chloride produced by

[1] Article II of this series, Table XII, footnote.

[2] A. A. Noyes, *Z. physik. Chem.*, 9, 609–18 (1892).

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the addition of salts with a common ion is in qualitative agreement with the principle of the constancy of the ionic solubility product, $(Tl^+)(Cl^-)$ = const. The relative solubilities at a given concentration of added salt are also in agreement with this principle. Thus the ionization values of the three chlorides increase in the order $BaCl_2$, KCl and HCl[1] and the solubilities of thallous chloride decrease in the same order. Similarly the ionization values increase and the solubilities decrease in the order

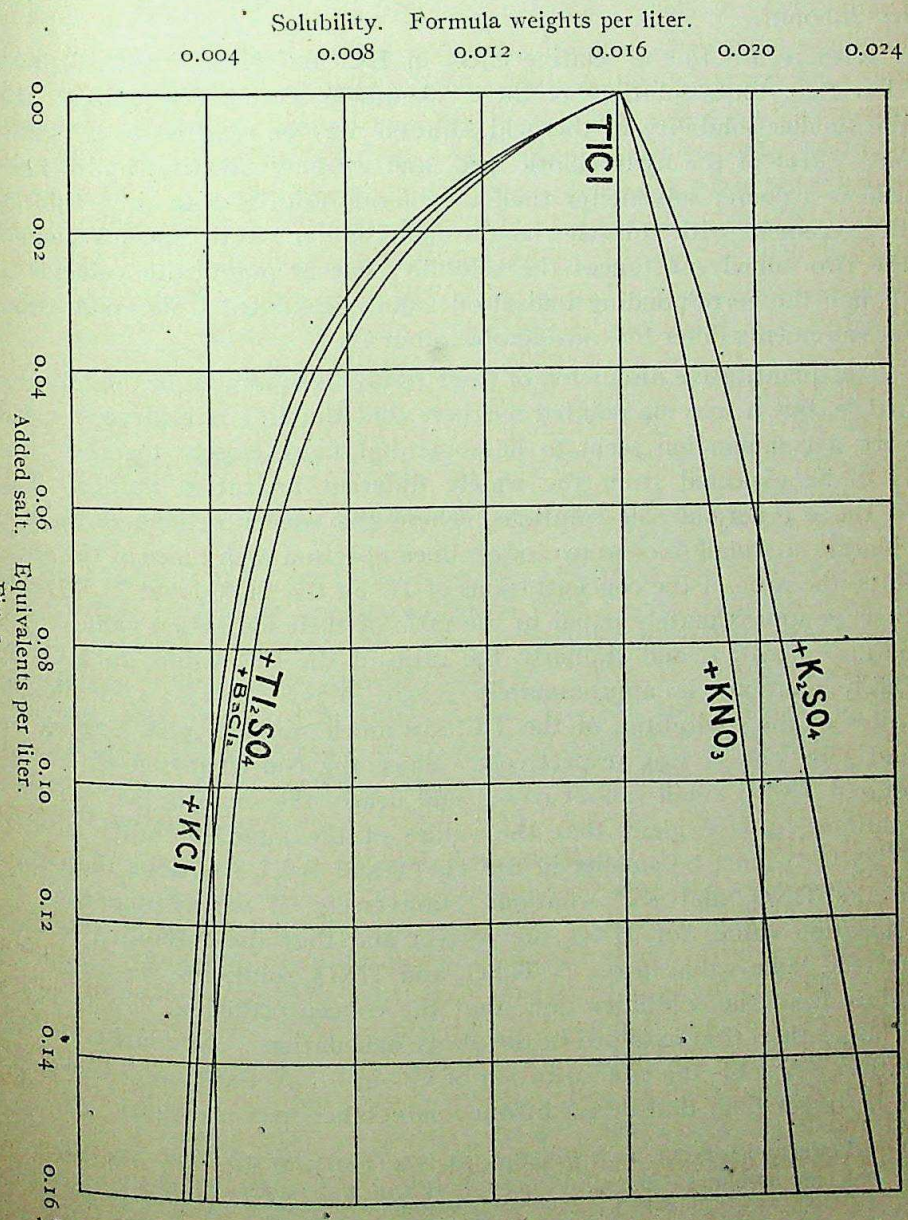

Fig. 1.

[1] Bray and Hunt, THIS JOURNAL, 33, 787 (1911).

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Tl_2SO_4, $TlNO_3$ and KCl. The striking agreement between the results obtained by Noyes with the three uni-univalent salts, KCl, NH_4Cl and NaCl, and with the six uni-bivalent salts indicates that the salts in each group are ionized to almost the same extent. This is in agreement with the results of conductance measurements, since in 0.1 normal solutions after correcting for viscosity the ionization values of KCl and NaCl differ by only 1 per cent. and those of $BaCl_2$, $CaCl_2$ and $MgCl_2$ differ by a slightly less amount.

With regard to the relative effect of HCl and KCl, if we accept the view that dilute solutions of these substances are equally ionized,[1] then the smaller solubility in the acid solution may be referred to a "salting out" effect of the hydrochloric acid, and we may say that hydrochloric acid is a poorer solvent for thallous chloride than is potassium chloride. In agreement with this view is the fact that at small concentrations of the two added substances the solubility curves practically coincide although the corresponding ionization values calculated from conductance measurements differ by considerable amounts.

The quantitative discussion of these results is presented in the following article, but it may be pointed out here that the different curves for salts with a common ion seem to lie somewhat more closely together than is to be expected from the widely different ionization values. Thus in the 0.1 normal salt solutions, where the concentrations of thallous chloride are small (0.0040 to 0.0047) in comparison with those of the added salts, the ratio of the concentrations of Tl^+ in the $TlNO_3$ and Tl_2SO_4 solutions is approximately equal to the ratio of their ionization values 0.792 : 0.614 = 1.29 : 1, and similarly the ratio of the Cl^- values in KCl and $BaCl_2$ solutions[2] is approximately 0.856 : 0.751 = 1.14 : 1, while the ratios of the solubilities of the TlCl are much smaller, 4.68/4.22 = 1.11 and 4.16/3.96 = 1.05 respectively. Since the concentration of the unionized TlCl is small (about 0.001) and nearly the same in each of these solutions, it is evident that the values of the ionic solubility product $(Tl^+)(Cl^-)$ must be smaller in the Tl_2SO_4 and $BaCl_2$ solutions than those in the $TlNO_3$ and KCl solutions. Conversely, if we assume that the ionization values for $TlNO_3$ are correct and that the solubility product has the same value in 0.1 *N* Tl_2SO_4 and $TlNO_3$ solutions, we would calculate from the solubility data that the concentration of Tl^+ in Tl_2SO_4 is larger than that assumed in the above calculations. Similarly, starting with 0.1 *N* KCl, the concentration of Cl^- in 0.1 *N* $BaCl_2$ would be found to be larger than that derived from conductance measurements.

[1] Lewis and Sargent, THIS JOURNAL, 31, 364 (1909); see also *Ibid.*, 33, 792.
[2] Kohlrausch and Grüneisen, *Landolt-Börnstein-Meyerhoffer, Tabellen*, 745.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 75.]

THE EFFECT OF SALTS ON THE SOLUBILITY OF OTHER SALTS. IV. QUANTITATIVE DISCUSSION OF THE SOLUBILITY OF UNI-UNIVALENT SALTS IN THE PRESENCE OF OTHER SALTS.

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In the two preceding articles, a number of examples of the effect of salts on the solubility of uni-univalent salts were presented, and it was pointed out that the solubility-lowering produced by salts with a common ion was qualitatively in agreement with the principle of the constancy of the ionic solubility product. The increase of solubility of thallous chloride in the presence of potassium sulfate is also in qualitative agreement with this principle, and undoubtedly furnishes a typical illustration of the effect of salts without a common ion. In the present article these examples will be discussed quantitatively by the method outlined in the introductory article of this series.

1. The Solubility of Thallous Chloride in the Presence of Various Salts.[1]

The values of the degree of ionization (γ), as given by the conductance ratio Λ/Λ_0, and of the ionization function $k = \frac{(B^+)(A^-)}{(BA)} = \frac{(C\gamma)(\gamma)}{(1-\gamma)}$ for a single salt, given in Tables III to VI of the preceding article, were plotted against the equivalent ion-concentration, $(\Sigma i) = C\gamma$. In the case of barium chloride the values of γ were calculated from the conductance data of Kohlrausch and Grüneisen[2] at 18°. From these plots were derived the data presented in Tables I and II. The method of extrapolation by which the values of γ and k above 0.01 N (Σi) for thallous chloride and above 0.1 N for $TlNO_3$ and Tl_2SO_4 were obtained was explained in the preceding article.

TABLE I.— VALUES OF 100 γ FOR VARIOUS SALTS AT 25°.

(Σi.)	KCl.	KNO_3.	$TlNO_3$.	TlCl.	$BaCl_2$.	K_2SO_4.	Tl_2SO_4.
0.01	93.7	93.2	92.4	91.0	87.6	85.9	81.7
0.02	91.7	90.7	89.25	86.95	83.8	81.3	74.8
0.03	90.3	88.85	86.9	83.95	81.2	78.1	70.2
0.05	88.2	86.05	83.2	79.4	77.8	73.9	64.0
0.07	86.65	83.9	80.4	75.9	75.6	71.0	59.8
0.10	84.9	81.3	77.0	71.75	73.0	67.9	55.4
0.15	82.9	78.3	72.5	66.5	70.0	64.2	50.4
0.20	81.4	75.7	69.1	62.5	68.0	61.5	46.7
0.25	80.0	73.4	66.2	59.4	....	....	....

[1] For the data see Article III of this series.

[2] *Landolt-Börnstein-Meyerhoffer, Tabellen*, 745.

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TABLE II.—VALUES OF 100 k FOR VARIOUS SALTS AT 25°.

(Σi).	KCl.	KNO_3.	$TlNO_3$.	TlCl.	K_2SO_4.	Tl_2SO_4.
0.01	14.8	13.70	12.15	10.10	6.10	4.46
0.02	22.2	19.50	16.60	13.30	8.70	5.96
0.03	28.0	23.85	19.90	15.70	10.70	7.06
0.05	37.3	30.8	24.8	19.25	14.15	8.89
0.07	45.5	36.4	28.7	22.00	17.15	10.41
0.10	56.2	43.5	33.4	25.40	21.20	12.41
0.15	72.8	54.1	39.5	29.75	26.90	15.23
0.20	87.7	62.3	44.6	33.6	31.90	17.52
0.25	100.3	68.9	49.1	36.6	...	...

The composition of the various solutions saturated with thallous chloride was calculated on the assumption that for each salt the values of γ in mixtures with a common ion, and of k in mixtures without a common ion depend only on the total equivalent ion-concentration (Σi). The results of the calculation are presented in the last ten columns of Table III. In the first column are given the names and concentrations of the

TABLE III.—COMPOSITION OF SATURATED TlCl SOLUTIONS.

(Concentrations in milliequivalents per liter.)

Added salt. ($\frac{1}{2}K_2SO_4$).	(ΣCl).	(Σi).	(K^+).	(Tl^+).	(Cl^-).	($\frac{1}{2}SO_4^{--}$).	($\frac{1}{2}K_2SO_4$).	($\frac{1}{2}Tl_2SO_4$).	(KCl).	(TlCl).	(Tl^+)(Cl^-).
0.0	16.07	14.32	0.0	14.32	14.32	0.0	0.0	0.0	0.0	1.755	204.9
19.96	17.79	20.33	16.73	13.60	15.52	14.81	2.30	2.85	0.93	1.338	211.0
49.96	19.42	51.96	38.80	13.16	16.61	35.35	9.47	5.14	1.69	1.120	218.3
99.89	21.37	85.03	72.17	12.86	17.87	67.16	25.19	7.54	2.53	0.966	229.7
299.6	26.00	200.9	188.5	12.45	20.77	180.2	106.6	12.78	4.46	0.768	258.6
($\frac{1}{2}Tl_2SO_4$).											
0.0	16.07	14.32	...	14.32	14.32	0.0	...	0.0	...	1.755	204.9
19.99	10.34	23.46	...	23.46	18.88	14.58	...	5.41	...	1.465	208.1
49.99	6.77	39.00	...	39.00	5.53	33.47	...	16.52	...	1.239	215.7
99.97	4.68	64.42	...	64.42	3.59	60.83	...	39.14	...	1.087	231.3

(KNO_3).	(ΣCl).	(Σi).	(K^+).	(Tl^+).	(Cl^-).	(NO_3^-).	(KNO_3).	($TlNO_3$).	(KCl).	(TlCl).	(Tl^+)(Cl^-).
0.0	16.07	14.32	0.0	14.32	14.32	0.0	0.0	0.0	0.0	1.755	204.9
20.00	17.16	32.42	17.84	14.58	14.91	17.51	1.25	1.24	0.91	1.343	217.4
49.97	18.26	57.65	42.87	14.78	15.50	42.15	5.46	2.36	1.64	1.124	229.1
99.98	19.61	97.08	82.11	14.97	16.23	80.85	15.56	3.67	2.41	0.968	243.0
300.0	231.3	238.3	233.0	15.34	18.20	220.1	72.9	7.02	4.16	0.775	279.2
($TlNO_3$).											
0.0	16.07	14.32	....	14.32	14.32	0.0	...	0.0	...	1.755	204.9
25.0	8.80	29.17	....	29.17	7.405	21.76	...	3.24	...	1.395	216.0
50.0	6.24	46.87	....	46.87	4.99	41.88	...	8.12	...	1.248	233.9
100.0	4.22	82.05	....	82.05	3.13	78.92	...	21.08	...	1.093	256.8

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Added salt. (KCl).	(ΣTl).	(Σi).	(K^+).	(Tl^+).	(Cl^-).	($\frac{1}{2}Ba^{++}$).	($\frac{1}{2}BaCl_2$).	(KCl).	(TlCl).	(Tl^+)(Cl^-).
0.0	16.07	14.32	0.0	14.32	14.32	...	...	0.0	1.755	204.9
25.0	8.69	29.88	22.58	7.30	29.88	...	...	2.42	1.390	218.1
50.0	5.90	48.85	44.15	4.70	48.85	...	...	5.85	1.204	229.6
100.0	3.96	88.40	85.5	2.90	88.40	...	...	14.5	1.061	256.3
200.0	2.68	166.54	164.8	1.74	166.54	...	...	35.2	0.94	290.0
($\frac{1}{2}BaCl_2$).										
0.0	16.07	14.32	....	14.32	14.32	0.0	0.0	...	1.755	204.9
25.0	8.98	28.00	....	7.59	28.00	20.41	4.59	...	1.392	212.5
50.0	6.18	44.30	....	4.98	44.30	39.32	10.68	...	1.203	220.6
100.0	4.16	77.97	....	3.11	77.97	74.86	25.14	...	1.052	242.4
200.0	2.82	142.7	....	1.89	142.7	140.8	59.2	...	0.93	270.0

added salts, and in the second the corresponding solubilities of thallous chloride (see Tables II and VII in the preceding article). In the third column are the equivalent ion-concentrations (Σi) $\times$ 10^3, and in the last two columns the concentrations of the unionized portion of thallous chloride (TlCl) $\times$ 10^3, and of the ionic solubility product (Tl^+)(Cl^-) $\times$ 10^6.

The specific conductances, L, of a number of these mixtures were calculated from the ionic concentrations by means of the following ionic conductances: Tl^+, 76.2; K^+, 74.8; Cl^-, 75.8; NO_3^-, 70.6; ½ $SO_4^=$, 80.0; and are compared in Table IV with the experimentally determined values (see Table II of the preceding article). The concentrations of the added salts are given in the first, fourth and seventh columns:

TABLE IV.—SPECIFIC CONDUCTANCES OF THE MIXTURES.

	1000 L.			1000 L.			1000 L.	
(½ K_2SO_4).	Meas.	Calc.	(½ Tl_2SO_4).	Meas.	Calc.	(KNO_3).	Meas.	Calc.
0.01998	4.644	4.647	0.01999	3.620	3.625	0.02000	4.807	4.811
0.04996	7.96	7.99	0.04999	6.05	6.07	0.04997	8.47	8.49
0.09989	13.02	13.10	0.09997	10.01	10.05	0.09998	14.18	14.22
						0.3000	34.62	34.77

The agreement between the calculated and the measured specific conductances is very satisfactory, but this is only another confirmation of the principle of the conductance of mixtures referred to in the introduction. The observed agreement is also a check on the accuracy of the experimental data and of the calculations. Another check on the calculations was obtained by comparing the values of $K = \frac{[(Tl^+)(Cl^-)]}{(TlCl)(\Sigma i)^{0.4}}$ given with those of $K = \frac{(C\gamma)^{1.6}}{C(1-\gamma)}$ given for thallous chloride solutions in Table IV of the preceding article. The agreement was complete.

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In Fig. 1*a* the values of the iodic solubility product and of the concentrations of the un-ionized portion of thallous chloride (Table III) are plotted as ordinates against the total ion-concentrations, $(\Sigma i) \times 10^3$, as abscissas. In order that the same ordinate scale might be used, the values plotted are $(Tl^+)(Cl^-) \times 10^5$ and $(TlCl) \times 10^4$. The diagram thus shows directly the relative variations of these two quantities with the ion-concentration.

In the curves on the right-hand side of the same diagram (Fig. 1*b*),

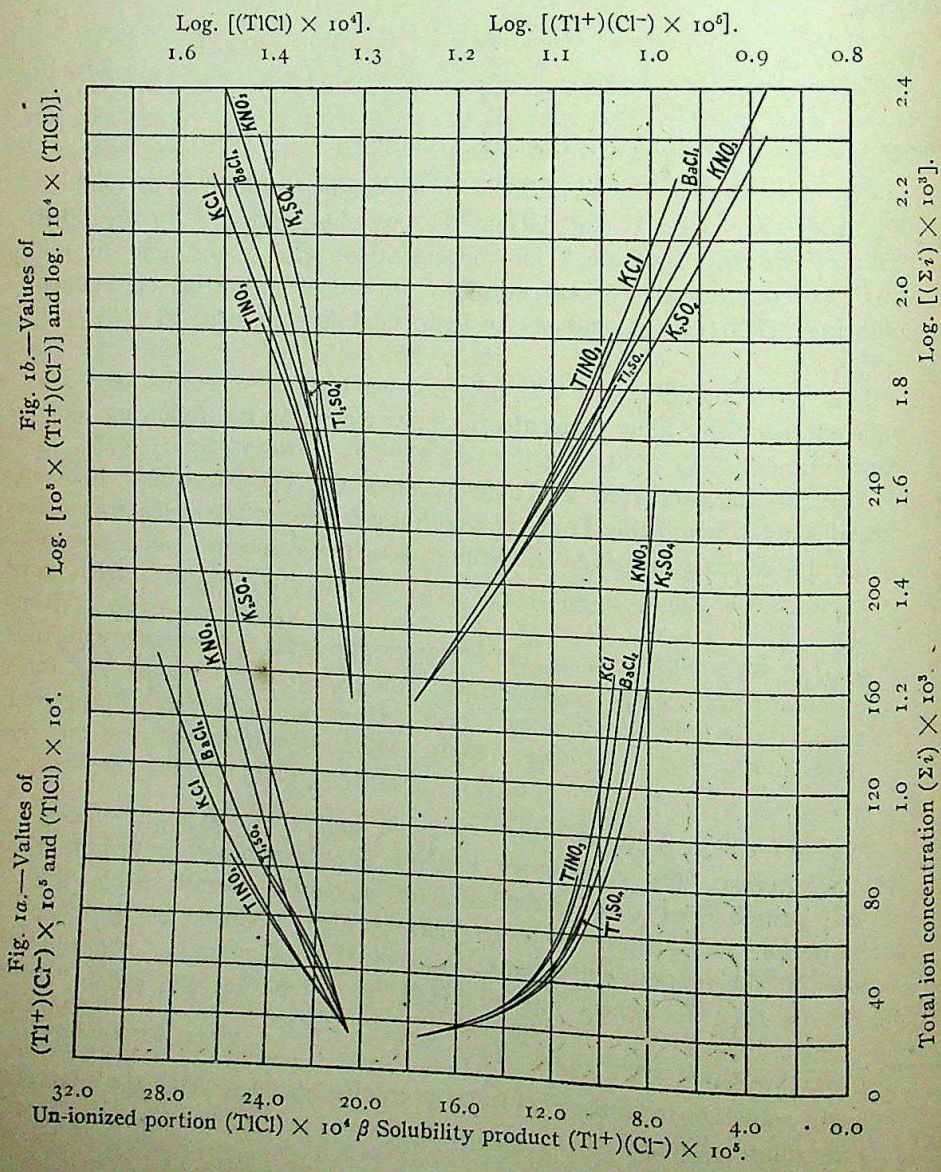

Fig. 1*a*.—Values of $(Tl^+)(Cl^-) \times 10^5$ and $(TlCl) \times 10^4$.

Fig. 1*b*.—Values of Log. $[10^3 \times (Tl^+)(Cl^-)]$ and log. $[10^4 \times (TlCl)]$.

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the logarithms of the quantities $[10^5(Tl^+)(Cl^-)]$ and 10^4 (TlCl) are plotted against the logarithm of 10^3 (Σi), the data themselves being given in Table V. The various curves have, of course, the same relative positions in the two cases, but the logarithmic plot has the advantage of showing the relationships in dilute solutions more clearly. The points corresponding to 0.02 N $BaCl_2$ and 0.05 N $TlNO_3$ were found to lie above the curves through the remaining points and were neglected, but the possible errors in the original experimental data were sufficiently great to account for such variations.

TABLE V.—DATA FOR THE LOGARITHMIC PLOT, FIG. 1*b*.

Added salt.	Log $10^3 \times$ (Σi).	Log $10^4 \times$ (TlCl).	Log $10^5 \times$ $(Tl^+)(Cl^-)$.	Added salt.	Log $10^3 \times$ (Σi).	Log $10^4 \times$ (TlCl).	Log $10^5 \times$ $(Tl^+)(Cl^-)$.
None.....	1.1559	1.2443	1.3115	K_2SO_4...	1.4819	1.1265	1.3243
Tl_2SO_4.....	1.3703	1.6158	1.3183		1.7157	1.0492	1.3401
	1.5911	1.0931	1.3339		1.9296	0.9850	1.3612
	1.8090	1.0362	1.3642		2.3030	0.8854	1.4126
$TlNO_3$.....	1.4649	1.1446	1.3345	KNO_3...	1.5108	1.1281	1.3373
	1.6709	1.0962	1.3690		1.7608	1.0508	1.3600
	1.9141	1.0386	1.4096		1.9871	0.9859	1.3856
					2.3771	0.8893	1.4459
$BaCl_2$.....	1.4472	1.1436	1.3274	KCl.....	1.4754	1.1430	1.3387
	1.6464	1.0803	1.3436		1.6889	1.0806	1.3610
	1.8919	1.0220	1.3846		1.9465	1.0257	1.4088
	2.1544	0.9685	1.4314		2.2215	0.9721	1.4624

It will be seen from the figure that neither the concentration of unionized TlCl nor the ionic solubility product is constant. In all cases, as the ion-concentration (Σi) increases, the value of (TlCl) decreases rapidly, and that of $(Tl^+)(Cl^-)$ increases steadily, although much more slowly. When we consider that (Σi) increases seventeen-fold (from 0.014 to 0.238), and that the results are based on experiments with uni-univalent and uni-bivalent salts with and without a common ion, it is very remarkable that the curves in each group lie as closely together as they do. The uniformity of the results therefore confirms the assumption that it is the total ion-concentration in the mixture which primarily determins the ionization of uni-univalent salts.

The figure shows the nature of the variation of (TlCl) and of $(Tl^+)(Cl^-)$ with (Σi). The curves obtained by plotting log (TlCl) against log (Σi) are more clearly linear than those obtained by plotting (TlCl) directly against (Σi), but the converse is true for the $(Tl^+)(Cl^-)$ curves. We will examin the logarithmic curves more closely on account of the following simple relationship between their slopes and the deviations from the law of mass action.

Any small portion of one of the curves may be considered to be a straight line whose equation is:

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$\log (TlCl) = m_u \log (\Sigma i) + \log k_u$ or $\log (Tl^+)(Cl^-) = m_i \log (\Sigma i) + \log k_i$. These equations when written in another form become:

$$(TlCl) = k_u(\Sigma i)^{m_u} \text{ and } (Tl^+)(Cl^-) = k_i(\Sigma i)^{m_i},$$

and the exponents m_u and m_i may be determined directly from the slopes of the tangents to the curves. It is obvious that the last two equations correspond to the general ionization function used in the calculations $\frac{(Tl^+)(Cl^-)}{(TlCl)} = K(\Sigma i)^{0.4}$, and that $m_i - m_u = 0.4$ and $k_i/k_u = K$. From the slope of the curves it is evident that in each case m_i is a small positive number which increases with increasing ion concentration, and that m_u is a negative number which is numerically greater than m_i and therefore appears to change less rapidly. The approximate values of m_i for each added salt at the ion concentrations $(\Sigma i) = 0.016$ and 0.100 normal are as follows:

TABLE VI.—VALUES OF THE EXPONENT m_i IN VARIOUS SALT SOLUTIONS.

$10^3(\Sigma i)$.	Log $10^3(\Sigma i)$.	K_2SO_4.	Tl_2SO_4.	$BaCl_2$.	KNO_3.	KCl.	$TlNO_3$.
16	1.20	0.03	0.03	0.03	0.07	0.07	0.07
100	2.00	0.12	0.17	0.18	0.12	0.19	0.20

The corresponding values of m_u were obtained by subtracting 0.40 from each of these numbers and were found to check with those derived directly from the (TlCl) curves. Thus the values of m_u at $(\Sigma i) = 0.016$ normal are —0.37 and —0.33 for the unibivalent and the uni-univalent salts, respectively.[1]

The values of m_i decrease with increasing ion-concentration and show a tendency to approach zero if the curves be produced toward zero concentration. This signifies that in the case of thallous chloride the

[1] Reference was made in the previous article to the possible inaccuracy of the ionization values of thallous chloride obtained by extrapolation, and to the calculation, by means of the expression $(C\gamma)^{1.55}/C(1-\gamma) = K'$, of values which were larger than those corresponding to the exponent $n = 1.60$. Thus at 0.1 normal γ was 0.766 instead of 0.751. The present calculations with K_2SO_4, Tl_2SO_4 and KNO_3 were repeated, using these higher values of γ for TlCl, and the data obtained were plotted in a diagram similar to Fig. 1. The results and curves did not differ in character from those presented above. The values of m_i were slightly larger than those given in Table VI, which was to have been expected, since $m_i - m_u = 0.45$ instead of 0.40.

A change in the ionization values of one of the added salts would, on the other hand, have specific effects on the results, but such effects are relatively small. Thus in the 0.1 normal KCl solution a 2 per cent. decrease in the degree of ionization of KCl causes a 2.0 per cent. decrease of (Σi), a 1.7 per cent. decrease of $(Tl^+)(Cl^-)$ and a 1.0 per cent. increase of (TlCl); and this would have the effect of only slightly lowering the (Tl^+) (Cl^-) curves and slightly raising the TlCl curves. It is therefore evident that the conclusions reached in this article would not be appreciably altered as a result of introducing a correction in the ionization values, such as that for viscosity, which is negligible in the very dilute solutions and does not exceed a few per cent. in the more concentrated ones.

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solubility product is more nearly constant in the dilute than in concentrated salt solutions, and furnishes some indications that the solubility product would be more exactly constant for a less soluble substance than thallous chloride.

From the result that in the dilute solutions m_u is much larger than m_i it follows that the deviations from the law of mass action in the ionization of thallous chloride are more largely due to the abnormal behavior of the un-ionized substance than to the abnormal behavior of the ions.[1] If we make use of the concept of activity, which was explained in the first article of this series, we may say that the activity coefficient of un-ionized TlCl (A_{TlCl}/C_{TlCl}) increases rapidly as the total ion-concentration increases and is proportional to its 0.37 to 0.33 power in dilute solutions. Similarly the product $\left(\frac{A_{Tl^+}}{C_{Tl^+}}\right)\left(\frac{A_{Cl^-}}{C_{Cl^-}}\right)$ decreases slowly, and is at first inversely proportional to the 0.03 to 0.07 power of the total ion concentration. If it is legitimate to distribute this effect equally upon the two ions, then the activity coefficient of each ion must decrease in the proportion in which the 0.015 to 0.035 power of the ion concentration increases. This is really only a small deviation from direct proportionality; and if, as seems reasonable, we assume the same law in a solution of a single uni-univalent salt where the concentration of each ion is equal to (Σi), then we may conclude that in dilute solutions (say 0.01 to 0.03 normal) the activity of each ion is nearly, but not quite, proportional to its concentration and increases somewhat less rapidly than the concentration. By similar reasoning, the increase in m_i with increasing ion concentration (shown in Table VI) leads to the similar conclusion that in more concentrated solutions of a single salt the activity coefficient (A/C) decreases more rapidly with increasing concentration of the salt.

This conclusion is in agreement with the results of electromotive force measurements of concentration cells. Lewis and Von Ende[2] have shown, namely, in connection with their work with the thallous-ion concentration cell, that the ratio A/C for the thallous ion is constant at low concentrations and shows a distinct decrease at 0.1 normal. The measurements of Jahn[3] on the chloride-ion concentration cell show a similar but more pronounced decrease of the activity coefficient of chloride ion.

In the foregoing discussion the general effects produced by added salts have been discussed, but a number of interesting specific effects

[1] Compare Lewis, *Proc. Am. Acad.*, **43**, 288 (1907); *Z. physik. Chem.*, **61**, 160 (1907).

[2] Lewis and Von Ende, THIS JOURNAL, **32**, 737 (1910). See also Bray and Mackay, *Ibid.*, **32**, 930, 1213 (1910).

[3] Jahn, *Z. physik. Chem.*, **33**, 545 (1900).

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may be easily seen by examining the figure and Table VI more closely. Thus from the effects produced by the first small portions of salts the six salts fall into two classes, the three uni-univalent salts, KNO_3, KCl and $TlNO_3$, and the three uni-bivalent salts, K_2SO_4, $BaCl_2$ and Tl_2SO_4. The initial portions of the three curves in each group practically coincide and the values of m_i are 0.07 and 0.03, respectively, for the uni-univalent and uni-bivalent salts. In each group of curves, as the solutions become more concentrated, the two curves corresponding to the salts with a common ion remain very close together, while the curve corresponding to the salt (KNO_3 or K_2SO_4) without a common ion diverges and always remains below the other two curves.

The fact that the effect of a uni-bivalent salt is consistently different from that of the corresponding uni-univalent salt shows that the mere presence of a bivalent ion has an effect on the ionization relations of thallous chloride which is somewhat different from that of an equivalent amount of the univalent ion. While such an effect is not improbable, it seems strange that the effect is in such a direction as to decrease m_i and thus make the activities of Tl^+ and Cl^- appear to be more nearly proportional to their concentrations in the uni-bivalent salt solution. On this account, and also to obtain if possible greater simplicity in the solubility relations of thallous chloride, it seems worth while to examin how the original assumptions may be altered in order to bring the two sets of effects into better agreement. This is the question which was referred to in the closing paragraph of the preceding article, and it was shown there that larger values would be calculated for the concentration of Cl^- in 0.1 N $BaCl_2$ and of Tl^+ in 0.1 N Tl_2SO_4 if the solubility product were assumed to be the same in 0.1 N Tl_2SO_4 as in 0.1 N $TlNO_3$ and the same in 0.1 N $BaCl_2$ as in 0.1 N KCl. A study of the $(Tl^+)(Cl^-)$ curves shows that we may now draw the corresponding general conclusion that these curves for the uni-bivalent salts would be raised if we assumed larger values for the total ion concentration in the uni-bivalent salt solutions. The corresponding effect on the concentration of the un-ionized TlCl would be to increase its value and thus bring the two groups of TlCl curves closer together. It is interesting to note that such a result suggests the presence of intermediate ions ($TlSO_4^-$ or $ClBa^+$) in the solutions of the uni-bivalent salts. The possibility of the existence of such ions has been mentioned in the introduction, and will be fully discussed by Dr. W. D. Harkins in a later article of this series.

2. The Solubility at 25° of $KClO_4$ in the Presence of KCl and K_2SO_4.[1]

The results of the calculations are given in Tables VII, the arrangement being the same as in Table III. The ionization values upon which the calculations are based were given in Table V of the second article

[1] Article II, A, of this series.

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of this series. It may be recalled that the ionization function there assumed for potassium perchlorate was

$$K = \frac{(C\gamma)^{1.5}}{C(1-\gamma)} = \frac{(K^+)(ClO_4^-)}{(KClO_4)(\Sigma i)^{0.5}}.$$

Table VIII contains the measured specific conductances of the mixtures and the values calculated[1] from the ionic conductances K^+, 74.8; ClO_4^-, 68.2; Cl^-, 75.8; and $\frac{1}{2}SO_4^{--}$, 80.0.

TABLE VII.—COMPOSITION OF SATURATED $KClO_4$ SOLUTIONS.
(Concentrations in milliequivalents per liter.)

Added salt.	Conc.	(ΣClO_4).	(Σi)=(K^+).	(ClO_4^-).	(Cl^-).	(KCl).	($KClO_4$).	(K^+)(ClO_4^-)
KCl.....	0.0	148.1	115.3	115.3	0.0	0.0	32.8	13290
	49.73	128.2	139.1	97.7	41.43	8.30	30.5	13590
	99.33	112.3	165.7	83.8	81.90	17.43	28.5	13890
					($\frac{1}{2}SO_4^{--}$).	($\frac{1}{2}K_2SO_4$).		
$\frac{1}{2}K_2SO_4$...	0.0	148.1	115.3	115.3	0.0	0.0	32.8	13290
	49.70	131.5	133.2	100.7	32.50	17.20	30.8	13410
	99.22	118.1	152.8	89.0	63.80	34.42	29.1	13600

TABLE VIII.—SPECIFIC CONDUCTANCES OF THE MIXTURES.

Added salt. (KCl).	1000 *L*. Meas.	1000 *L*. Calc.	Added salt. ($\frac{1}{2}K_2SO_4$).	1000 *L*. Meas.	1000 *L*. Calc.
0.04973	20.29	20.21	0.04970	19.46	19.43
0.09933	24.84	24.31	0.09922	22.63	22.60

It will be seen from the table that as the ion-concentration increases, the concentration of un-ionized $KClO_4$ decreases steadily and that the ionic solubility product (K^+)(ClO_4^-) increases steadily, though much less rapidly. This is similar to what was found above with thallous chloride, but in the present case the relations between (Σi) and ($KClO_4$) and between (Σi) and (K^+)(ClO_4^-) are almost linear. On account of the small range of these experiments, the corresponding logarithmic curves (shown in Fig. 2) are also almost linear. In order that the same scale might be used in drawing the different curves the increase of log (K^+)(ClO_4^-) and the decrease of log ($KClO_4$) have been plotted against the increase of log (Σi). The data for Fig. 2 are given in Table IX.

TABLE IX.—DATA FOR THE LOGARITHMIC PLOT (FIG. 2).

Added salt.	Increase of log (Σi).	Increase of log (K^+)(ClO_4^-).	Increase of log ($KClO_4$).
KCl.....	0.0815	0.0097	—0.0316
	0.1575	0.0192	—0.0610
K_2SO_4.....	0.0627	0.0039	—0.0273
	0.1223	0.0100	—0.0520

[1] For the significance of the agreement of the calculated specific conductances with the measured values see the discussion following Table IV, above. In the present instance the disagreement in the 0.1 *N* KCl experiment is undoubtedly due to an error in the measured value, since this was not checked by a duplicate measurement.

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Since the curves in the figure are nearly linear it follows that the exponents m_i and m_u (in the equations $(K^+)(ClO_4^-) = k_i(\Sigma i)^{m_i}$ and $(KClO_4) = k_u(\Sigma i)^{m_u}$) are nearly constant in the range of the experiments. When the added salt is potassium chloride $m_i = 0.11$ and $m_u = -0.39$, while for small additions of potassium sulfate $m_i = 0.07$ (and increases with increasing concentration) and $m_u = -0.43$. These results are thus seen to be very similar to those obtained with thallous chloride and may be interpreted in the same way.

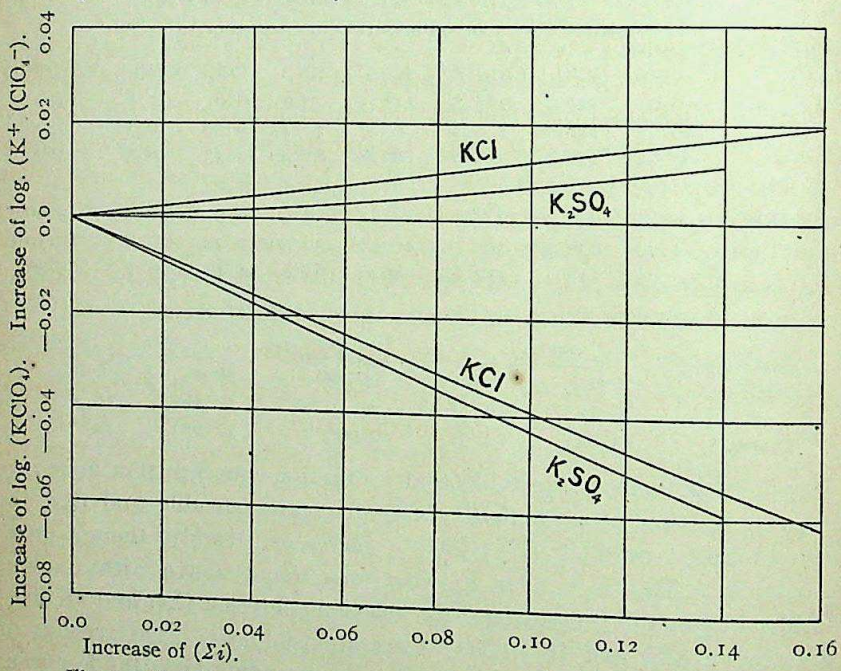

Fig. 2.—Variation of log. $(K^+)(ClO_4^-)$ and log. $(KClO_4)$ with log. (Σi).

A comparison with Table VI shows that the values of m_i in the $KClO_4$ experiments are greater than the corresponding values for small additions of salts in the TlCl experiments. This is undoubtedly due to the fact that $KClO_4$ is a much more soluble salt than TlCl, and corresponds to the increase, shown in Table VI, of m_i with increasing ion concentration and to the former conclusion that the activity coefficient (A/C) for univalent ions decreases with increasing ion concentration. Furthermore, if we consider the solubility product we see that it is more nearly constant in the thallous chloride experiments for small additions of salts than in the experiments with the more soluble substance, potassium perchlorate, so that we have further evidence that the principle of the constancy of the solubility product will hold in the case of difficultly soluble substances for small additions of salts.

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3. The Solubility of $TlClO_3$ and Tl_2SO_4 in the Presence of Each Other.[1]

The results of the calculations are presented in Table X:

TABLE X.—COMPOSITION OF SATURATED $TlClO_3$ AND Tl_2SO_4 SOLUTIONS.
(Concentrations in equivalents per liter.)

($\Sigma\frac{1}{2}SO_4$).	(ΣClO_3).	(Σi)=(Tl^+).	(ClO_3^-).	($\frac{1}{2}SO_4^=$).	($\frac{1}{2}Tl_2SO_4$).	($TlClO_3$).	(Tl^+)(ClO_3^-).
0.0	0.1340	0.1073	0.1073	0.0	0.0	0.0267	0.01152
0.1366	0.1058	0.1511	0.0817	0.694	0.0672	0.0241	0.01234
0.1928	0.0	0.1064	0.0	0.1064	0.0864	0.0	.....

An examination of the first two lines[2] of the table shows that with increasing ion concentration the concentration of the un-ionized $TlCl_3$ decreases rapidly, and the ionic solubility product (Tl^+)(ClO_3^-) increases less rapidly. The values of the exponents m_i and m_u were calculated to be 0.20 and —0.30 respectively. The value of m_i is larger than that found in the $KClO_4$ experiments, but is about the same as the values found in the TlCl experiments in the more concentrated salt solutions (see Table VI). The three sets of results studied in this article are thus seen to yield corresponding results.

Discussion of the Results.

The results reached in the cases here investigated, that the concentration of the un-ionized substance in the saturated solution rapidly decreases with increasing concentration, is in perfect agreement with the conclusions drawn by Arrhenius and Stieglitz from the solubility determinations with the silver salts of certain organic acids in the presence of salts with common ions. It may therefore be accepted as a general principle.

The evidence in favor of regarding as a general law the increase of the solubility product with increasing ion-concentration is somewhat less conclusive; but the results presented in this article and the data on the electromotive force of concentration cells support such a conclusion. Stieglitz's calculations, it is true, show a general increase of the solubility product for the silver salts of organic acids, but the increase is much less rapid than in the TlCl experiments, even in the case of the silver salts which are more soluble than thallous chloride. For the silver salts of about the same or smaller solubility than thallous chloride the solubility product remains almost exactly constant over a large range of concentration of the added salts. We must therefore conclude for the present

[1] Article II, B. The ionization values are given in Table XI of this article.

[2] The last two lines of the table show the effect on the solubility of the uni-bivalent salt Tl_2SO_4 produced by $TlClO_3$, a uni-univalent salt with a common ion. In this case the concentration of the un-ionized Tl_2SO_4 is seen to decrease rapidly with increasing ion-concentration and the solubility product (Tl^+)^2($SO_4^=$) was found to increase rapidly. Additional more comprehensive examples will be presented in later articles of this series.

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that the solubility product for uni-univalent salts remains nearly constant or increases steadily with increasing ion-concentration, and that the increase will probably be more marked the greater the solubility of the salt.

The inconstancy of the ionic solubility product has recently been discussed by Hill,[1] who concluded that there is a decrease and not an increase with increasing concentration of added electrolyte. His experiments show that the solubility of thallous chloride decreases rapidly in very concentrated solutions of acetic acid, and that the solubility of tetramethylammonium iodide decreases rapidly in very concentrated solutions of potassium hydroxide. The solubility product must decrease in these cases with increasing concentration of the added substance; but it is very doubtful whether Hill is justified in drawing general conclusions from these two cases, since acetic acid at least is not a typical strong electrolyte and since the behavior in dilute solutions has not been carefully examined. It seems more probable that these experiments indicate the mutual insolubility of acetic acid and thallous chloride, and of tetramethylammonium iodide and potassium hydroxide. That such "solvent effects" must be taken into consideration has been shown in a striking manner by Kendall[2] in a recent article.

Summary.

In this article the effects of six typical salts on the solubility of thallous chloride, of two salts on the solubility of potassium perchlorate, and of one salt on the solubility of thallous chlorate have been discussed quantitatively by the method described in the introduction to this series of articles. This method consists essentially in calculating, with the aid of ionization values derived from conductance, the concentration of the un-ionized portion and the product of the concentrations of the ions of the salt with which the solution is saturated for the case when it is present alone and for cases in which another salt is simultaneously present.

This "un-ionized" concentration and this "solubility product" should, according to the mass action law, be constant in any saturated solution. The actual variations of these quantities in the different cases are shown in the last two columns of Tables III, VII, and X, and in Fig. 1*a* of this article. In every case the un-ionized concentration (BA) decreases markedly and the solubility product $(B^+)(A^-)$ increases slightly, as the total concentrations of the salts and of the ions in the saturated solution increase.

A study of these variations by means of the logarithmic plots of Fig. 1*b* and 2 shows that they can be expressed approximately as a function

[1] Hill, THIS JOURNAL, 32, 1186 (1910).

[2] Kendall, *Proc. Roy. Soc.*, 85, 200 (1911).

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of the total ion-concentration (Σi) in the solution by the exponential equations,

$$(BA) = k_u(\Sigma i)^{m_u} \text{ and } (B^+)(A^-) = k_i(\Sigma i)^{m_i},$$

in which k_u, k_i, m_u, and m_i are constants, which were separately determined for each substance in the presence of each added salt. These expressions are evidently closely related to the empirical dilution law $(B^+)(A^-)/(BA) = K(\Sigma i)^{2-n}$, K being equal to k_i/k_u and the exponent $2-n$ equal to $m_i - m_u$. In the case of thallous chloride, where the range of the concentrations of the added salts was very large, these exponential expressions do not fully express the results. As shown by the curvature of the logarithmic graphs, different values of the exponent m_i or m_u must be assumed at different concentrations.

The values of m_i and m_u were found to be as follows:

			m_i.	m_u.
TlCl	+ uni-univalent salts	at (Σi) = 0.016....	0.07	—0.33
	+ uni-bivalent salts	at (Σi) = 0.016....	0.03	—0.37
	+ uni-univalent salts	at (Σi) = 0.100....	0.12 to 0.20	—0.28 to —0.20
	+ uni-bivalent salts	at (Σi) = 0.100....	0.12 to 0.18	—0.28 to —0.22
$KClO_4$	+ KCl	at (Σi) = 0.12	0.11	—0.39
	+ K_2SO_4	at (Σi) = 0.12	0.07	—0.43
$TlClO_3$	+ Tl_2SO_4	at (Σi) = 0.12....	0.20	—0.30

It will be seen that the values of m_i at the small concentration 0.016 normal are small and less than those at the higher concentrations. This seems to justify the conclusion that the solubility product would be practically constant in the case of less soluble salts in the presence of small quantities of other salts.

The fact that the values of m_i are much smaller than those of m_u at small concentrations shows that the deviation from the theoretical dilution law $(B^+)(A^-)/(BA) = k$ is mainly due to abnormal behavior of the un-ionized substance and only secondarily to abnormal behavior of the ions.

In terms of the activity concept, these results indicate that the ratio of the activity to the concentration of univalent ions is nearly constant below 0.016 normal, but that above this concentration it decreases with increasing concentration at first slowly and then more rapidly. The corresponding ratio for the un-ionized portion, on the other hand, increases very rapidly with increasing concentration throughout the whole range of concentration investigated.

The nearly uniform effect on the un-ionized concentration and on the solubility product exerted by the salts of the two different valence types and by those with and without a common ion confirms the original assumption that the ionization relations of uni-univalent salts are primarily determined by the total equivalent ion-concentration. There are,

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however, consistent differences of secondary order in the effects of the different kinds of salts, and especially between the uni-uni- and uni-bivalent salts.

In conclusion, I take pleasure in thanking Professor A. A. Noyes for his assistance in connection with this investigation.

(CONTRIBUTIONS FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE LAWS OF "CONCENTRATED" SOLUTIONS. III.[1] THE IONIZATION AND HYDRATION RELATIONS OF ELECTROLYTES IN AQUEOUS SOLUTION AT ZERO DEGREES: A. CESIUM NITRATE, POTASSIUM CHLORIDE AND LITHIUM CHLORIDE.

BY EDWARD W. WASHBURN AND DUNCAN A. MACINNES.

Received August 28, 1911.

1. Purpose and Outline of the Investigation.

In undertaking a systematic extension of our knowledge of aqueous solutions of strong electrolytes into the region of "concentrated" solutions, it is natural to begin the study with the simplest type of such electrolytes, the uni-univalent salts. The salts of this type range from those such as cesium nitrate and iodide, which are slightly or not at all hydrated in solution, to those of which lithium chloride is an example, which are combined with considerable amounts of the solvent. The present investigation includes the two salts cesium nitrate and lithium chloride, which represent extremes in this respect, together with one salt, potassium chloride, which occupies an intermediate position.

For investigating the condition of these salts in solution the freezing-point method was adopted. As pointed out in a previous paper,[3] this method possesses the disadvantage that one is obliged to change two variables simultaneously, the concentration and the temperature. This difficulty can be avoided either (1) by combining measurements of heat of dilution with those of freezing-point lowering, or (2) by replacing the freezing-point method by the method of vapor-pressure lowering. For higher temperatures the latter alternative is preferable and a parallel

[1] Contributions Nos. 1 and 2 of this series appeared in THIS JOURNAL, 32, 653 and 1636 (1910), and 33, 1461 (1911). Owing to the fact that the author was given no opportunity to correct the page proof of article No. 2, it is necessary to note the following corrections: p. 1462, for G. N. Lewis[4] read G. N. Lewis[1]; p. 1472, line 1, for (10) read (12); p. 1467, for (see p. —) read (see p. 1471); p. 1473, Table IV, for 19° read 18°, and for f_0 read η_0; p. 1463, Note 2, next to last line, the figure 7 is omitted.

[2] Presented at the Indianapolis meeting of the Society, June 29, 1911. Abstract of a thesis presented by Mr. MacInnes to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] *Technology Quarterly*, 21, 379–80 (1908).

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investigation at 25° by that method is now in progress in this laboratory. For temperatures in the neighborhood of 0°, however, the former method involves fewer difficulties for the same degree of accuracy and was accordingly adopted.

In addition to the freezing-point data, measurements of the conductances and relative viscosities of the solutions at 0° were also made so that the degrees of ionization of the salts could be calculated. The necessary heat of dilution data will be determined in connection with another investigation as the laboratory did not possess a sufficiently accurate calorimeter at the time this investigation was made.

The results which are tabulated in the following pages include complete conductance, viscosity, density, and freezing-point data for solutions of potassium and lithium chlorides up to normal and for cesium nitrate up to half-normal. In so far as reliable data were already available in the literature, they have been employed and have been supplemented by our own measurements in order to make them complete within the above concentration range. The question of accuracy has been carefully considered and an estimate of the probable accuracy is indicated after each of the final values given in the tables. Although in some instances this estimate is to a certain extent arbitrary it is believed that the limits indicated will usually be found too large rather than too small.

2. Purification of Materials.

Cesium Nitrate.—The method of purification used was that described by Wells.[1] Cesium carbonate (Kahlbaum) was dissolved in nitric acid, iodine and hydrochloric acid added in the proportion necessary to form $CsCl_2I$ and the mixture heated. The orange colored crystals which separated upon cooling were filtered from the mother liquor and dried as far as possible by suction. The crystallization was repeated three times from hot hydrochloric acid (1 to 1). The final product was heated over a flame in a casserole to remove the iodine and excess of chlorine and the resulting cesium chloride was converted into nitrate by four evaporations with pure nitric acid. The cesium nitrate thus obtained was crystallized four times from conductivity water and the final product dried in an air bath. The product thus obtained when examined spectroscopically showed no lines except those of cesium.

Lithium Chloride.—Kahlbaum's pyridine was dried by boiling with caustic potash and then distilled. The distillate was heated with an excess of carefully dried lithium chloride (Kahlbaum) and filtered. The filtrate was placed in a distilling flask, the pyridine driven off by heating, and the residue twice evaporated to dryness with pure hydrochloric

[1] *Am. J. Sci.*, 43, 17 (1892).

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acid.[1] The resulting product was then dried at 150°. On examination it was found to be spectroscopically pure.

Potassium Chloride.—Kahlbaum's purest potassium chloride was recrystallized four times from conductivity water and dried by suction. It was always fused immediately before use.

Water.—All the water used in this investigation was conductivity water obtained from the special still[2] in this laboratory. It was collected hot and kept in thoroughly steamed bottles of "Non-sol." glass. The specific conductance of the water at 0° averaged 0.4×10^{-6} mhos.

3. Methods of Measurement.

(*a*) *The Conductance Measurements.*—A slide wire bridge of the roller type described by Kohlrausch and Holborn and furnished by Hartmann and Braun was employed in the conductance measurements. The platinum-iridium slide wire had a length of about 3 meters, the smallest scale division being 3 mm. It was calibrated against the standard resistances of the Physics Laboratory, using the method described by Kohlrausch and Holborn.[3] This calibration was repeated from time to time, whenever it became necessary to clean the wire.

The resistance coils were Hartmann and Braun's highest grade manganin coils with the high resistances wound according to the Chaperon principle. The coils were compared with the standards of the Physics Laboratory and found to be correct well within the limits of error of our measurements. A small Kohlrausch condenser[4] was used in parallel with the resistance box or the cell in all the measurements.

The alternating current was furnished by a small induction coil provided with an adjustable resistance in series with its primary coil. It was connected to the bridge through a commutating switch. Commutation either of the coil or the telephone was, however, found to be without influence upon the readings.

With the above arrangement complete silence was obtained in the telephone at the null point with all except the most dilute and the most concentrated solutions. Readings could be repeatedly checked to 1 part in 5000.

The cells, which were made of Jena Geräteglas, were of the pipet type[5] shown in Fig. 1. The internal diameter was about 15 mm. and the horizontal electrodes were 10 mm. in diameter. Three cells were employed with electrodes 75 mm., 15 mm., and 2 mm. apart, respectively. The first cell was employed for salt solutions ranging in concentration

[1] Method of Kahlenberg and Krauskopf, THIS JOURNAL, 30, 1104 (1908).

[2] The form of the still is described by Noyes and Coolidge, *Proc. Am. Acad.*, 39, 190 (1908).

[3] "Leitvermögen der Elektrolyte," p. 47.

[4] Kohlrausch and Holborn, p. 60.

[5] Similar to the cell designed by Kraus, see THIS JOURNAL, 31, 732 (1909).

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between N and 0.1 N, the second for those between 0.1 N and 0.005 N, while the third was used for the most dilute solutions. The electrodes were coated with platinum black and cleaned in the usual manner.

The conductance capacities at 0° of the first two cells were determined by measurements with normal and tenth-normal solutions of potassium chloride prepared exactly as directed by Kohlrausch and Holborn[1] and the values used for the specific conductances of these solutions at 0° were 0.06541 and 0.007150 mhos, respectively. The constants found by measurements with solutions prepared at two different times are as follows:

	Date, Oct. 19, 1910.		Date, Jan. 1, 1911.	
Solution.	N.	0.1 N.	N.	0.1 N.
Cell 1	3.423	3.425	3.423	3.424
Cell 2	...	0.6222	...	0.6222

The conductance capacity (0.01592) of the smallest cell was determined from that of the second cell by measurements with the same dilute solution in both. The conductance of the water was determined in a cell of the usual Arrhenius type with unplatinized electrodes 3 cm. in diameter and about 2 mm. apart. The measurements of the conductance of the water used gave results agreeing within about 2 per cent., which is sufficiently accurate.

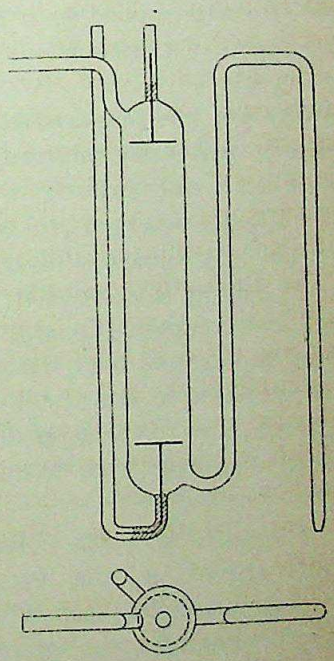

Fig. 1.

All conductance measurements were made at 0°, a large Dewar tube filled with a mixture of pure water and finely chopped ice (made from distilled water) being used as the constant temperature bath. This mixture was kept in constant motion by an electrically driven stirrer. Investigation of this bath with a delicate thermometer showed a temperature constant to 0.001° in all parts of the bath. The pipet cells were placed in the bath in such a manner that only the body of the cell (*i. e.*, the portion containing the solution) was immersed, the stem projecting over the edge of the Dewar tube and serving to hold the cell in position. Short leads of heavy copper wire connected the cell with the bridge, and their resistance was compensated by similar leads connecting the resistance box to the other arm of the bridge.

[1] "Leitvermögen der Elektrolyte," p. 76. 74.422 grams of fused potassium chloride in 1000 grams of solution (weights in air).

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(*b*) *The Density Measurements.*—The pycnometers used were of the Ostwald-Sprengel type, with a glass cap ground on the end of one capillary and a small bulb blown in the upper part of the other to allow for expansion of the liquid contained. This was necessary, as the pycnometer was filled at 0° and weighed at room temperature. A second pycnometer was used as a counterpoise when weighing. The capacity of the pycnometers was about 25 cc. All densities are at 0°, referred to water at 4°.

(*c*) *The Freezing-Point Measurements.*—The freezing-point measurements were made by the Equilibrium Method.[1] The freezing-point vessel was a silvered Dewar vacuum tube having a capacity of 200 cc. The Dewar tube was closely surrounded by, but not in contact with, a bath composed of a mixture of fine ice and water. Through openings in the cover were inserted a Beckmann thermometer, a glass stirrer, and a tube, *T*, which was used for withdrawing solution. In order to prevent the removal of small particles of ice, this tube was drawn out to a capillary at its lower end and to prevent the solution from rizing in this tube, air pressure was applied to it until air began to bubble from the tip. The upper end of the tube was then closed by means of a rubber tube and pinchcock.

Pure ice was prepared by placing test tubes containing conductivity water in a freezing mixture. The ice collected on the walls of the tubes, and the central portions, containing any impurities present, were poured off. The ice was then broken into small lumps in a mortar which had been previously chilled by filling it with fine ice. These lumps were placed in the Dewar tube until it was about three-fourths filled, and the solution, having about the concentration desired, was cooled to its freezing point and poured over the ice. The cover carrying the Beckmann thermometer, stirrer, and the tube *T* was then put in place, the tip of the tube *T* being close to the bulb of the thermometer but not touching it. The whole apparatus was surrounded with an asbestos shield to protect it from air currents.

Determination of the Concentration at Equilibrium.—The solution was slowly stirred and the temperature noted. During this time the thermometer was lightly tapped by an electrical hammer. As soon as a constant temperature was attained the tapper was stopped and the temperature accurately noted (R_1). A portion of about 10 cc. was then drawn off through the tube *T* and rejected. Then without allowing the solution filling the tube to fall back, the tube was connected to the stem of the conductivity cell (Fig. 1) and after filling the cell with solution, the connection with the tube *T* was closed by means of the pinchcock and the cell removed. After this, the thermometer was again read (R_2)

[1] For reference to previous work with this method see Ostwald-Luther, "Physicochemischen Messungen," Ed. 3, p. 281.

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with the idea of using the mean between this reading and the first one, R_1, but in no instance was any difference observed in these two readings.

To determin the concentration of the solution in the conductivity cell, its specific conductance at 0° was carefully determined as described above, and the concentration obtained by interpolation from conductance measurements on solutions of known concentrations.

Calibration of the Thermometer.—The Beckmann thermometer was carefully calibrated for irregularities of bore by the usual method of a moving mercury thread. The value of a degree in terms of the standard hydrogen thermometer was found by comparison with a Beckmann thermometer newly standardized by the National Bureau of Standards. For two weeks before the beginning of the investigation and when not in use until its completion, the thermometer was kept in an ice bath in order to protect it from large changes of temperature. Each time the thermometer was used, its zero point was determined with pure ice and water. The readings of the thermometer were always made with a rizing meniscus, with the tapper temporarily stopped, and at a definit and constant 100m temperature, the last precaution rendering stem exposure corrections unnecessary, except in the case of the more concentrated solutions of lithium chloride. For these solutions a Beckmann thermometer standardized at the Bureau of Standards was employed and the necessary corrections for stem exposure were applied.

(*d*) *The Viscosity Measurements.*—The viscosimeter was of the Ostwald type but with the upper ends of the two tubes connected by a device similar to that employed by Archibald, McIntosh and Steele,[1] so as to prevent the entrance of warm air into the apparatus during the measurement. The upper and lower bulbs, the centers of which were at a difference of level of 16 cm., had capacities of 6.0 and 40 cc. respectively. The capillary was 10.7 cm. long and 0.055 cm. in diameter. A specially constructed support maintained the viscosimeter in a vertical position in the vigorously stirred mixture of fine ice and water which served as the constant temperature bath. The time of flow was measured by a tested stop-watch reading $^1/_5$ second.

Before each series of measurements the viscosimeter was cleaned by filling it with concentrated nitric acid containing a few drops of alcohol and allowing it to remain over night. It was then rinsed several times, first with conductivity water and then with the solution, and allowed to drain completely. A definit quantity of the solution was introduced with a pipet. The water value was determined immediately before or after that of each solution. When necessary, the solutions were

[1] *Z. physik. Chem.*, 55, 129 (1907), see also Ostwald-Luther, "Physico-chemischen Messungen," Ed. 3, p. 233.

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filtered through a previously washed hardened filter to insure freedom from small dust particles.

The potassium chloride solutions were made up from weighed quantities of the fused salt and water. The concentrations of the lithium chloride solutions were determined by conductance measurements.

Standardization of the Viscosimeter.—For a viscosimeter of the above type the relative viscosity of any solution is given by the expression

$$\frac{\eta}{\eta_0} = \frac{(D-\lambda)t}{(D_0-\lambda)t_0}P \qquad (1)$$

in which t and t_0 are the times of flow of solution and water respectively, D and D_0 their respective densities, and λ the density of air at the same temperature. P is a correction factor, which is equal to unity if the viscosimeter obeys Poiseuille's Law exactly, but which, in general, differs slightly from unity and must be determined for each instrument.

Grüneisen[1] has shown that the correction factor, P, for any solution in a given viscosimeter is given by the equation

$$P = \frac{1+\varphi(t_0)}{1+\varphi\left(\frac{t\eta}{D\eta_0}\right)} \qquad (2)$$

and that the function φ has the form $e^{b/t_0^n}-1$, the constants b and n being determined by the dimensions of the viscosimeter.

For a viscosimeter having the dimensions given above, the exponent n may without error be taken equal to unity.[2] Equation (2) consequently becomes

$$P = e^{hb} \quad (3),$$

where h is written for the expression

$$\frac{\frac{t\eta}{D\eta_0}-t_0}{\frac{t_0 t\eta}{D\eta_0}}.$$

Since the exponent hb is a small quantity the equation may be written, finally,

$$P = 1 + hb. \qquad (4)$$

In order to obtain the constant, b, for any viscosimeter it is only necessary to determin the time of flow of a solution for which η/η_0 is accurately known. For this purpose we employed a cesium nitrate solution having the composition 3.3488 grams of $CsNO_3$ per 1000 grams of water. The careful determinations of Merton[3] give this solution a relative viscosity of $\eta/\eta_0 = 0.9246$ at 0°.

Using this solution in our viscosimeter we obtained the following

[1] *Wiss. Abhandl. Phys. Tech. Reichsanstalt*, 4, 241 (1904).
[2] Grüneisen, *Loc. cit.*, p. 159.
[3] *J. Chem. Soc.*, 97, 2454 (1910).

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values : $t_o = 317.8$ sec., $t = 277.5$ sec., $D = 1.0618$ and hence $h = -0.0010$ and $b = 2.8$.

(*e*) *The Weights.*—The set of weights used in this investigation was standardized at the Bureau of Standards. All the numerical data given in this paper are based upon *weights in vacuo*.

4. The Conductance and Density Data.

Cesium Nitrate.—The results of the density and conductance measurements with this salt are shown in Table I.

Cesium nitrate solutions of definit concentrations were prepared by weighing the fused salt into well steamed, glass stoppered, Erlenmeyer flasks of Jena glass, adding conductivity water and again weighing. From these solutions a series of more dilute solutions was prepared by weight. Solutions made directly from the salt are marked by asterisks in Table I. Solution No 6 was prepared from a different sample of cesium nitrate as a check. The cesium nitrate for this solution was prepared from Kahlbaum's cesium chloride by four evaporations with pure concentrated nitric acid and three crystallizations of the product from conductivity water at 0°, using centrifugal drainage.

TABLE I.—CESIUM NITRATE SOLUTIONS AT 0.000°.

Conductance and Density Data.

No.	Moles of salt per 1000 grams of H_2O. n'.	Density 0°/4°. D.	Corrected specific conductance $\times 10^6$. $\kappa \times 10^6$.	Cell No.
1	0.5389*	1.07705	30900.0	1
2	0.4282	1.0630	26350.0	1
3	0.4427*	1.0623	26110.0	1
4	0.3346	1.0475	20420.0	1
5	0.3078	1.0425	18980.0	1
6	0.2498*	....	15740.0	1
7	0.2383*	....	15060.0	1
8	0.1612	1.0222	10700.0	1
9	0.1529	1.0215	10170.0	1
10	0.1059*	....	7262.0	2
11	0.09314*	1.0145	6461.0	2
12	0.05962	1.0074	4315.0	2
13	0.04666	1.0056	3397.0	2
14	0.01730	1.00206	1336.0	2
15	0.008877	1.0015	702.2	2
16	0.003940	....	318.0	3
17	0.001737	....	141.3	3
18	0.0004414	....	36.44	3
19	0.0002115	....	17.61	3

*Specific conductance of the water $= 0.44 \times 10^{-6}$ mhos.

The more dilute solutions, 0.02 N and less, were found to be readily contaminated by contact with the air and by standing for some time in the flasks. To overcome these sources of error the flasks, previously

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weighed, were filled with fresh, hot, conductivity water directly from the still, and allowed to stand over night. The following day they were rinsed thoroughly and then weighed, together with the required quantity of conductivity water. A portion of a freshly prepared solution of known concentration was then added and the flask and contents reweighed. By this method the flasks were not dried before the solution was made up and the impurities in the adhering water were not retained in the flask. The quantities of water and solution were adjusted so that but a small air space remained below the stopper.

The cell, after thorough cleaning and soaking out with hot, conductivity water, was filled first with the most dilute solution and afterward with the other solutions in order of their strengths.

TABLE II.—LITHIUM CHLORIDE SOLUTIONS AT 0.000°.

Conductance and Density Data.

No.	Moles of salt per 1000 grams of H_2O. n'.	Density 0°/4°. D.	Corrected specific conductance $\times 10^6$. $\kappa \times 10^6$.	Cell No.
1	0.9990	1.0233	39200.0	1
2	0.8218	1.0193	33390.0	1
3	0.6187	1.0151	26230.0	1
4	0.3659	1.0093	16650.0	1
5	0.3561	1.0088	16260.0	1
6	0.2144	1.0054	10270.0	1
7	0.07702	1.0021	3988.0	2
8	0.04120	1.0009	2210.0	2
9	0.03337	1.0007	1801.0	2
10	0.01646	....	917.2	2
11	0.008322	....	474.2	3
12	0.002027	....	118.8	3
13	0.001039	....	61.33	3
14	(0.0005144)	....	(30.66)	3

Specific conductance of the water = 0.49×10^{-6} mhos.

Lithium Chloride.—Table II shows the results of the density and conductance measurements with this salt. The series of solutions of known concentrations below 0.6 N was made by dilution, as described above, of the two solutions whose analyses are given below:

Solution.	Weight of sample.	Wt. AgCl.	Moles LiCl per 1000 grams H_2O.
1	25.184	2.1754	0.6026
	25.115	2.1714	0.6032
2	99.608	0.4755	0.03331
	99.555	0.4756	0.03331

The concentrations of solutions Nos. 1, 2 and 3 were determined by analysis in the same manner.

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5. The Viscosity Data.

Table III shows the results obtained in the viscosity measurements. The "uncorrected" η/η_0 values are shown in column IV. The next column contains the correction factors, obtained as explained in section 3. It will be noted that the maximum correction is only 0.2 per cent. The final corrected values are shown in the last column.

TABLE III.—VISCOSITY DATA AT 0°.

No.	n'.	$D_0°/4°$. Interpolated.	η/η_0 (uncorr.).	P.	η/η_0 (corr.).
		Potassium Chloride.			
1.....	0.9991	1.0473	0.9307	0.9977	0.9286
2.....	0.8010	1.0383	0.9410	0.9981	0.9392
3.....	0.6020	1.0293	0.9533	0.9985	0.9519
4.....	0.5160	1.0249	0.9569	0.9987	0.9557
5.....	0.4063	1.0197	0.9654	0.9989	0.9643
6.....	0.3015	1.0146	0.9752	0.9992	0.9744
7.....	0.2118	1.0104	0.9864	0.9996	0.9860
8.....	0.1042	1.0051	0.9944	0.9998	0.9842
		Lithium Chloride.			
1.....	0.9776	1.0228	1.1240	1.0015	1.1257
2.....	0.8710	1.0205	1.1133	1.0014	1.1150
3.....	0.6036	1.0151	1.0813	1.0011	1.0825
4.....	0.3508	1.0088	1.0481	1.0006	1.0488
5.....	0.3247	1.0082	1.0434	1.0006	1.0441
6.....	0.2540	1.0066	1.0337	1.0005	1.0342
7.....	0.1077	1.0029	1.0125	1.0002	1.0127

6. The Freezing-Point Data.

Cesium Nitrate.—The data obtained with this salt are shown in Table IV. The strongest solution studied was in equilibrium with both ice and solid cesium nitrate, so that the eutectic point for this salt is —1.254° and the concentration of the saturated solution is $n' = 0.4370$ moles of $CsNO_3$ per 1000 grams of water.

All of the data shown in Table IV were treated by the method of Least Squares and the following equation obtained:

$$\Delta t = (3.426\, n' - 1.862\, n'^2 + 1.373\, n'^3) \pm 0.0019^0. \qquad (5)$$

The "probable error," 0.0019°, is that given by the relation, $P.E. = 0.675\sqrt{\Sigma D^2/10}$, where ΣD^2 is the sum of the squares of the deviations of the observed values from those calculated by means of the above equation. These calculated values, together with the deviations, are also shown in Table IV.

Lithium Chloride.—Of the data shown in Table IV, the first seven values are those of Jahn[1] corrected to the basis of the 1911 atomic weight table. The remaining values were obtained in this laboratory.

[1] *Z. physik. Chem.*, 50, 135 (1904).

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TABLE IV.—FREEZING-POINT DATA.

No.	n'.	Δt obs.	Δt calc.	Diff.
		Cesium Nitrate.		
1	0.0185	0.067°	0.064°	—0.003°
2	0.0525	0.174	0.175	—0.001
3	0.1296	0.418	0.416	—0.002
4	0.1595	0.507	0.505	—0.002
5	0.1855	0.582	0.580	—0.002
6	0.2169	0.666	0.669	+0.003
7	0.2729	0.824	0.824	0.000
8	0.2816	0.852	0.848	—0.004
9	0.3212	0.949	0.954	+0.005
10	0.4148	1.203	1.200	—0.003
11	0.4370	1.254	1.256	+0.002
		Lithium Chloride.		
1	0.0251	*0.091°*	0.090°	—0.001°
2	0.0506	*0.179*	0.178	—0.001
3	0.0749	*0.265*	0.265	0.000
4	0.1515	*0.526*	0.527	+0.001
5	0.2042	*0.709*	0.709	0.000
6	0.2548	*0.888*	0.888	0.000
7	0.2966	*1.038*	1.038	0.000
8	0.3350	1.177	1.177	0.000
9	0.4301	1.529	1.528	—0.001
10	0.5580	(2.005)	2.012	+0.007
11	0.8218	3.053	3.054	+0.001
12	0.9990	3.790	3.789	—0.001

In order to estimate the accuracy of the data, the values of n' were plotted against values of $^1/_3(\Delta t/n' - 3.3)$ and the best smooth curve passed through the points by means of a spline. From this curve values of Δt corresponding to the first six values of n' given in Table IV were then read off. Since the remainder of the curve could not be distinguished from a straight line, linear interpolation was employed for the remaining values of n'. The Δt values thus obtained ($\Delta t_{calc.}$) are shown in Table IV, together with their deviations from the corresponding observed values. A deviation of 0.001° amounted to about 2 mm. on the scale employed.

7. Equivalent Conductances at Zero Concentration.

To determin the Λ_0 value for each salt, extrapolation was made by the method of A. A. Noyes. Values of the equivalent resistance, $1/\Lambda$, were plotted against the corresponding values of $(C\Lambda)^{n-1}$, and the value of the exponent n adjusted until a straight line was obtained. For cesium nitrate, values of these functions for the concentrations, 0.0002115, 0.0004414, 0.001737, 0.003940 and 0.008877 were employed and were calculated from the specific conductances of solutions Nos. 15, 16, 17, 18 and 19 of Table I. The value of the exponent, n, was 1.50. The

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Λ_0 value thus obtained (84.0) is estimated to be known with a precision of about two units in the first decimal place.

For lithium chloride the value, $\Lambda_0 = 60.3 \pm 0.3$, was obtained in the same manner. The solutions employed for this extrapolation were Nos. 11, 12 and 13 of Table II. The value of the exponent n in the expression $(C\Lambda)^{n-1}$ was 1.53.

To potassium chloride Noyes and Coolidge[1] assign the value $\Lambda_0 = 81.4$. This was derived from the experimental data of Whetham[2] and of Kahlenberg.[3] Using the same data Johnston[4] found $\Lambda_0 = 81.9$. As the difference is considerable we decided to repeat this extrapolation and proceeded as follows:

Using Kohlrausch and Maltby's data for potassium chloride at 18°, values of $1/\Lambda$ were first plotted against values of $(C\Lambda)^{0.5}$, giving the 6 points corresponding to the concentrations 1, 2 and 5 ten-thousandths and 1, 2 and 5-thousandths normal respectively. By use of a spline, a smooth curve was made to pass through all six points. This curve, which was not far from a straight line, crossed the axis of zero concentration at the point $\Lambda_0 = 130.1$, thus giving the same value which Kohlrausch and Maltby obtained. The values 130.0 and 130.2 would, moreover, have been clearly inconsistent with the rest of the curve, so that this method of extrapolation leads, in the case of potassium chloride at all events, to the same Λ_0 value as does the one employed by Kohlrausch.

The same method of procedure was also employed with the data of Whetham and those of Kahlenberg for this salt at 0°. Only the values in the concentration interval 0.0002 to 0.03 normal were employed. Two values obtained by Kohlrausch and Holborn,[5] for the concentrations 0.01 and 0.02 normal, respectively, were also included. Using the spline, it was found that a perfectly smooth curve could be made to pass through eight of the nine points obtained from Whetham's data. The deviation in the case of the one point corresponded to an error of only 0.05 per cent. in Λ. The same curve also passed through *both* of the points obtained from the data of Kohlrausch and Holborn. Up to 0.01 normal the curve was exactly linear and it crossed the axis at a point corresponding to $\Lambda_0 = 81.0 \pm 0.1$. The points obtained from Kahlenberg's data were irregular. The "best" straight line through them did not coincide with the other line and led to a value of Λ_0 somewhere between 81.6 and 81.9. A study of the experimental methods of the two investigators indicates that Whetham's measurements were conducted with much greater care and accuracy than those of Kahlen

[1] Carnegie Inst., Pub. No. 63, 47 (1907).
[2] *Z. physik. Chem.*, 33, 351 (1900).
[3] *J. Phys. Chem.*, 5, 348 (1901).
[4] THIS JOURNAL, 31, 1012 (1909).
[5] *Loc. cit.*, p. 204.

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SUMMARY OF DATA AT ROUND CONCENTRATIONS.

TABLE V.—CESIUM NITRATE SOLUTIONS AT 0.000°. (1911 ATOMIC WEIGHTS.)

Moles of salt per 1000 grams of water. n'.	Freezing-point depression. $\Delta t \pm 0.002°$.	Density $D_{0°/4°}$. $\pm 0.01\%$.	Relative viscosity. η/η_0. $\pm 0.03\%$.	Equivalent conductance Λ. $\pm 0.1\%$.	$\frac{\Lambda}{\Lambda_0}$. $\pm 0.25\%$.	$\frac{\Lambda\eta}{\Lambda_0\eta_0}$. $\pm 0.25\%$	$\frac{\Lambda}{\Lambda_0}\left(\frac{\eta}{\eta_0}\right)^{0.826} = r$. $\pm 0.30\%$.	$\frac{100(1+r)n'}{55.53+(1+r)n'} = \frac{100N'}{}$.
0.00000	0.000	0.9999	1.0000	(84.0±0.2)	1.0000	1.0000	1.0000	0.0000
0.02500	0.086	1.0030	0.9960	75.19	0.8948	0.8912	0.8939	0.0852
0.05000	0.168	1.0061	0.9905	72.94	0.8680	0.8597	0.8651	0.1676
0.07500	0.247	1.0104	0.9846	70.96	0.8445	0.8315	0.8376	0.2476
0.10000	0.325	1.0136	0.9796	69.32	0.8249	0.8080	0.8148	0.3258
0.2000	0.622	1.0278	0.9613	65.18	0.7757	0.7456	0.7543	0.6279
0.3000	0.897	1.0414	0.9446	63.04	0.7502	0.7087	0.7190	0.9202
0.4000	1.160	1.0565	0.9291	60.88	0.7245	0.6731	0.6849	1.1992
0.5000	(1.419±0.005°)	1.0710	0.9138	59.31	0.7058	0.6449	0.6582	1.4712

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berg, and this fact, together with the close concordance of his values with one another and with those of Kohlrausch and Holborn, indicates that 81.0 is the most probable Λ_0 value for potassium chloride at 0°, and, if Whetham's values are as accurate as they appear to be, the uncertainty in this value should not exceed 0.2 per cent.

8. Summary of Data at Round Concentrations.

Tables V, VI and VII contain the values of the freezing-point lowerings, densities, relative viscosities, and equivalent conductances of the solutions of the three salts at round concentrations. *All* of the data in these tables are based upon the 1911 atomic weight table. In cases where the data of other observers have been employed the necessary correction to this basis has been made.

Cesium Nitrate (Table V).—The Δt values (column II) are those given by the empirical equation (5) derived in Section 6. A solution having the concentration $n' = 0.5$, to which a freezing-point lowering of $1.419 \pm 0.005°$ is assigned, is, however, a supersaturated solution. This value for Δt was obtained from equation (5), but as this involves an extension of the equation beyond the limits for which it was derived a graphical extrapolation was made as a check. For this purpose a graph of equation (5) was made on cross-section paper. A spline was then made to pass through all of the points plotted, the highest point being that for the concentration 0.4370. The portion of the spline projecting beyond this was then grasped by one man while a second man sighted along the spline from the opposit end and the first man shifted the position of the upper end until, in the judgment of the second man, it made a smooth curve with the remainder of the spline. The value of Δt for the concentration 0.5000 was then read off. This process was repeated five times with three different men and the following results obtained: 1.417°, 1.420°, 1.417°, 1.418°, 1.418°; mean, 1.4178°, which checks the value calculated from equation (5) within 0.002°. Owing, however, to the fact that it is an extrapolated value, a somewhat larger probable error has been assigned to it.

The relative viscosities shown in column IV were obtained by graphical interpolation from the accurate data of Merton.[1]

The density and equivalent conductance values are based upon the data of Table I. The values of Λ were calculated by the equation

$$\Lambda = \frac{\kappa(1000 + n'M)}{1000\, n'D}, \qquad (6)$$

in which κ is the specific conductance and M the equivalent weight.

Potassium Chloride (Table VI).—The Δt values for concentrations up to and including $n' = 0.5$ are taken from the critical compilation

[1] *Loc. cit.*

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SUMMARY OF DATA AT ROUND CONCENTRATIONS.

TABLE VI.—POTASSIUM CHLORIDE SOLUTIONS AT 0.000°. (1911 ATOMIC WEIGHTS.)

Moles of salt per 1000 grams of water. n'.	Freezing-point depression. $\Delta t \pm 0.005°$.	Density $D_{0°/4°}$. $\pm 0.05\%$.	Relative viscosity η/η_0. $\pm 0.1\%$.	Equivalent conductance Λ. $\pm 0.2\%$.	$\frac{\Lambda}{\Lambda_0}$. $\pm 0.25\%$.	$\frac{\Lambda\ \eta}{\Lambda_0 \eta_0}$. $\pm 0.3\%$.	$\frac{\Lambda}{\Lambda_0}\left(\frac{\eta}{\eta_0}\right)^{0.90} = \gamma$ $\pm 0.4\%$.	$\frac{100(1+\gamma)n'}{55.53+(1+\gamma)n'} = \frac{}{100\,N'}$.
0.0000	0.000°	0.9999	1.000	81.0±0.2	1.000	1.000	1.000	0.000
0.0250	0.089	1.0012	0.9985	75.54	0.9326	0.9312	0.9313	0.0868
0.0500	0.175	1.0025	0.9971	73.68	0.9096	0.9070	0.9073	0.1714
0.0750	0.262	1.0037	0.9960	72.47	0.8947	0.8911	0.8915	0.2458
0.1000	0.345	1.0049	0.9945	71.58	0.8837	0.8788	0.8793	0.3373
0.2000	0.680	1.0098	0.9866	69.51	0.8581	0.8467	0.8477	0.6611
0.3000	1.009	1.0146	0.9743	68.63	0.8473	0.8256	0.8276	0.9776
0.4000	1.335	1.0194	0.9649	67.92	0.8385	0.8091	0.8119	1.289
0.5000	1.658	1.0242	0.9574	67.32	0.8312	0.7958	0.7990	1.594
0.6000	1.983	1.0289	0.9517	66.96	0.8267	0.7867	0.7906	1.898
0.8000	2.635	1.0380	0.9394	66.23	0.8176	0.7681	0.7733	2.491
1.000	3.287	1.0472	0.9286	65.51	0.8087	0.7510	0.7569	3.067

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SUMMARY OF DATA AT ROUND CONCENTRATIONS.

TABLE VII.—LITHIUM CHLORIDE SOLUTIONS AT 0.000°. (1911 ATOMIC WEIGHTS.)

Moles of salt per 1000 grams of water n'.	Freezing-point depression. Δt.		Density $D_{0°/4°}$. ±0.05%.	Relative viscosity η/η_0. ±0.2%	Equivalent conductance Λ. ±0.1%.	$\frac{\Lambda}{\Lambda_0}$. ±0.35%.	$\frac{\Lambda\eta}{\Lambda_0\eta_0}$. ±0.4%	$\frac{\Lambda}{\Lambda_0}\left(\frac{\eta}{\eta_0}\right)^{0.94}=r$. ±0.4%.	$\frac{100(1+r)n'}{55.53+(1+r)n'}$, $=100\,N'$.
0.0000	0.000°		0.9999	1.000	60.3±0.3	1.000	1.000	1.000	0.000
0.0250	0.090		1.0005	1.0030	54.54	0.9043	0.9070	0.9069	0.0858
0.0500	0.177		1.0012	1.0060	52.96	0.8781	0.8834	0.8830	0.1693
0.0750	0.265	±0.002°	1.0020	1.0088	51.90	0.8606	0.8682	0.8677	0.2516
0.1000	0.351		1.0025	1.0118	51.07	0.8468	0.8568	0.8562	0.3331
0.2000	0.694		1.0050	1.0260	48.39	0.8023	0.8232	0.8219	0.6519
0.3000	1.049		1.0074	1.0408	46.67	0.7738	0.8054	0.8034	0.9649
0.4000	1.416		1.0100	1.0557	45.30	0.7511	0.7931	0.7905	1.273
0.5000	1.791		1.0123	1.0692	44.00	0.7296	0.7802	0.7771	1.575
0.6000	2.174	±0.004°	1.0146	1.0819	42.89	0.7112	0.7695	0.7659	1.872
0.8000	2.966		1.0186	1.1072	41.43	0.6869	0.7606	0.7560	2.467
1.000	3.792		1.0234	1.1282	40.02	0.6636	0.7487	0.7434	3.044

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published recently by Noyes and Falk[1] and are based chiefly upon the data of Jahn. The value for $n' = 1$ is that of Raoult[2] and the values for $n' = 0.6$ and 0.8 are interpolated.

The density data are interpolated from the results of Freund.[3]

The viscosity data are based upon the values of Table III.

Of the equivalent conductance values those for $n' = 0.025$, 0.1 and 1.0 are based upon the data of Kohlrausch and Holborn.[4]

The remaining values were interpolated from the data of Kahlenberg.[4]

Lithium Chloride (Table VII).—The Δt values are those obtained by interpolation as explained on page 1696.

The density and equivalent conductance values are based upon the data in Table II, and the viscosity values upon those in Table III.

9. Comparison of the Three Salts.

The Degree of Ionization.—In order to estimate the degrees of ionization of the salts, the expression $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$ was employed. The deduction of this relation, the evidence in its favor and the derivation of the numerical values of the "fluidity exponent," m, have all been discussed in the preceding communication of this series.[4] The values of γ thus obtained are shown in column VIII of Tables V, VI and VII.

It will be noted that the values for cesium nitrate are the lowest and those for potassium chloride the highest of the three salts. The figures in columns VI and VII, respectively, permit a comparison with the values for γ which one would obtain (1) by neglecting the viscosity influence and (2) by taking the fluidity exponent equal to unity.

The Mole Fractions and Freezing-Point Lowerings.—In order to compare the effects of the three salts upon the freezing point, values of the mole fraction, N', for each salt were plotted against the corresponding values of the freezing-point lowering. The mole fractions were calculated by means of the equation

$$N' = \frac{(1 + \gamma)n'}{1000/18 + (1 + \gamma)n'}, \qquad (7)$$

and the values of $100\,N'$ are given in the last column of Tables V, VI, and VII.

For an "ideal solution" the relation connecting the freezing-point lowering and the mole fraction, N', of the solute was deduced in the first paper of this series.[5] If water is the solvent and if the solution is only moderately concentrated, the following equation is a sufficiently exact numerical statement of this relation.

[1] THIS JOURNAL, 32, 1011 (1910).
[2] *Z. physik. Chem.*, 27, 659 (1898).
[3] *Ibid.*, 66, 508 (1909).
[4] *Loc. cit.*
[5] *Loc. cit.*, equation 127, p. 667 (and p. 1636).

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$$N' = 0.00969\ (\Delta t - 0.00425\Delta t^2). \qquad (8)$$

A comparison of this equation with the freezing point data for non-electrolytes has already been made.[1] It will be recalled that the data for the simpler alcohols and for chloral hydrate were in good agreement with the above equation.[2] Of the other non-electrolytes for which data were available, the deviation, with one exception, was always in the direction which would result if the solute were hydrated in solution. The only pronounced deviation in the opposite direction, a deviation which would occur if the solute were partially associated, was found in the case of glycocoll, a substance for which association, due to partial neutralization, is to be expected.

A solute, which gives freezing-point lowerings in accordance with equation (8) and hence presumably one which is neither associated, dissociated, nor hydrated, will be called a "normal solute." Fig. 2 shows the curve of a "normal solute," together with the curves given by the tnree salts. In this figure values of the mole per cent. 100 N' are taken as ordinates and values of Δt as abscissas. The dotted lines crossing these curves are iso-concentration lines, that is, lines showing the positions of equal values of n' for the three salts. The same relations are shown more exactly in Table VIII. This table

TABLE VIII.—THE THREE SALTS COMPARED WITH A "NORMAL SOLUTE".

n'.	0.05	0.1	0.2	0.3	0.5	1.0
			$CsNO_3$.			
$\Delta t_{obs.}$	0.168°	0.325°	0.622°	0.897°	1.419°	(2.6)°
$\Delta t_{n.s.}$	0.173	0.336	0.650	0.953	1.528	(2.9)
$\Delta t_{obs.} - \Delta t_{n.s.}$	—0.005	—0.011	—0.028	—0.056	—0.109	—(0.3)
			KCl			
$\Delta t_{obs.}$	0.175°	0.345°	0.680°	1.009°	1.658°	3.287°
$\Delta t_{n.s.}$	0.177	0.348	0.684	1.013	1.656	3.209
$\Delta t_{obs.} - \Delta t_{n.s.}$	—0.002	—0.003	—0.004	—0.004	0.002	0.078
			LiCl.			
$\Delta t_{obs.}$	0.177°	0.351°	0.694°	1.049°	1.791°	3.792
$\Delta t_{n.s.}$	0.175	0.344	0.675	1.000	1.636	3.183
$\Delta t_{obs.} - \Delta t_{n.s.}$	0.002	0.007	0.019	0.049	0.155	0.609

shows ($\Delta t_{obs.}$) tne freezing-point lowerings of each salt for the concentrations (n') given at the top of the table; and also the corresponding values ($\Delta t_{n.s.}$) which a "normal solute" would give at the concentration $(1 + \gamma)\ n'$, the values for γ being those given in column VIII of Tables V, VI and VII.

If both the ions and un-ionized molecules of the salts were "normal

[1] *Technology Quarterly*, 21, 373 (1908).

[2] *E. g.*, for a 1.089 weight-normal solution, equation (8) gives $\Delta t = 1.987°$. For a solution of ethyl alcohol of this concentration Raoult (*l. c.*) found $\Delta t = 1.990°$.

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solutes" the corresponding values of Δt would all be identical and the four curves of Fig. 2 would coincide. That they are far from doing so is evident from the figure and from the data of Table VIII. The difference in the behaviors of electrolytes in their effect upon the freezing point is a well known fact, which has been emphasized recently by the

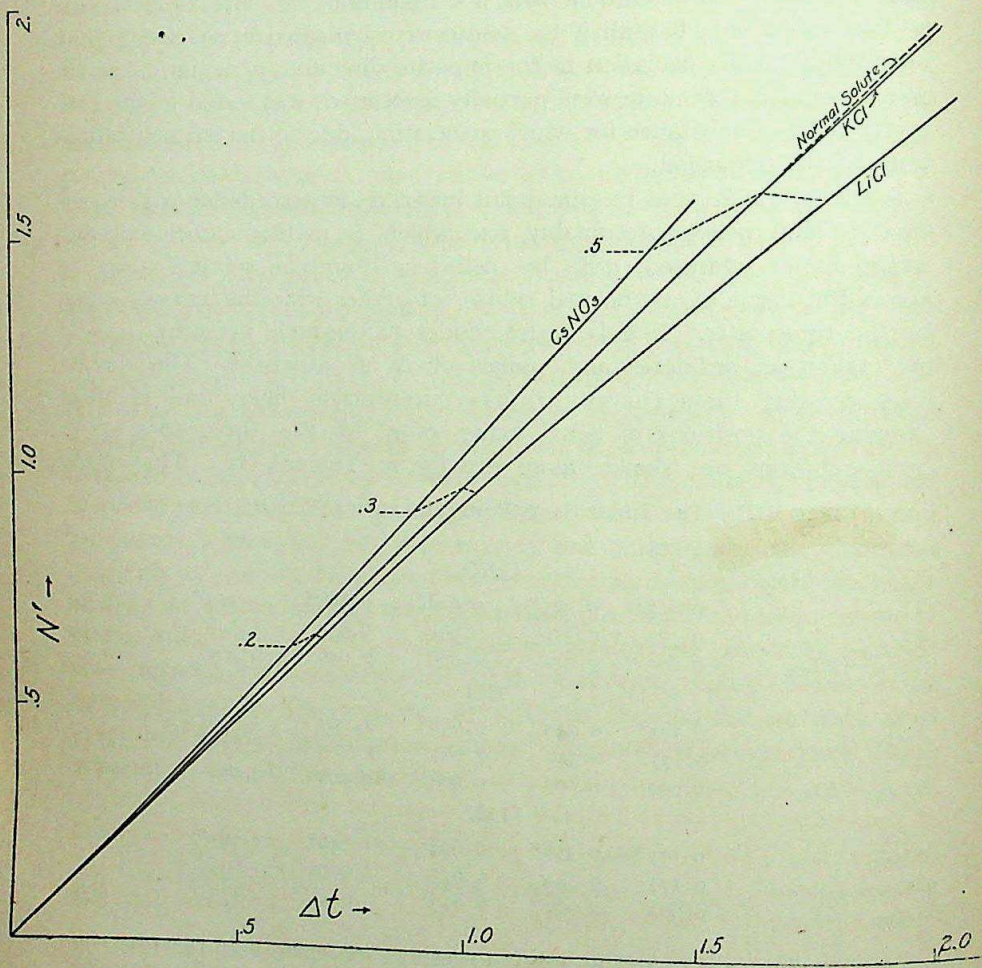

Fig. 2.

extensive investigations of H. C. Jones and his co-workers. Jones attributes this difference to the different degrees of hydration of the electrolytes and attempts to calculate the approximate degrees of hydration by assuming that the difference between the observed freezing-point lowering and that required by the laws of the infinitly dilute solution is due entirely to hydration. That such a procedure is theoretically

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unjustifiable and leads to improbable and even absurd results has already been pointed out.[1]

It was hoped that the present investigation might lead to some less objectionable method of estimating the degree of hydration of an electrolyte in solution and, as explained in the introduction, the two salts cesium nitrate and lithium chloride were included in the first experiments because, while both belong to the simplest type of electrolytes, they represent opposit extremes as regards their degrees of hydration. Let us therefore examin the results of the investigation, with this object in mind.

Turning to Fig. 2 and to Table VIII, and considering first the behavior of potassium chloride, it will be noted that, up to a concentration of about 0.5 mole of potassium chloride per 1000 grams of water, the behavior of this salt is (within the experimental error) in exact agreement with the assumptions, (1) that it is unhydrated, and (2) that both the ions and the un-ionized molecules are "normal solutes," each producing upon the freezing point the same effect as would be produced by an equal number of alcohol molecules, for example.[2]

Are these two assumptions, therefore, to be considered as justified? This question must seemingly be answered in the negative: (1) because we have independent evidence[3] that the ions of potassium chloride are hydrated and (2) because if ions and un-ionized molecules *both* behave as "normal solutes;" the mass-action law becomes a thermodynamic necessity;[4] while we know that it is not even approximately obeyed by this salt. It seems probable, therefore, that there are two influences at work in the case of strong electrolytes. One of these, which is probably closely connected with the "abnormal" behavior which produces the deviation from the mass-action law, operates to produce too small a freezing-point lowering.[5] The other, the hydration influence, naturally operates to produce too great a depression of the freezing point, and in the case of potassium chloride it happens that these two effects exactly counterbalance each other and make the salt apparently exhibit the behavior of a normal solute.

Turning now to cesium nitrate, it is evident that if deviation from the

[1] *Technology Quarterly*, 21, 367 (1908). For example, in a liter of a 4 molal solution of H_2CrO_4, Jones finds that "41.75 mols" (four significant figures!) of water are "combined" with the solute, and this in spite of the fact that *a liter of a 4 molal H_2CrO_4 solution contains only 36.5 moles of water altogether.*

[2] This is, of course, equivalent to the statement that the degree of ionization of this salt as calculated from conductivity data agrees exactly with the value calculated from the freezing-point lowering.

[3] *Loc. cit.* *Technology Quarterly*, and THIS JOURNAL, 31, 322 (1909).

[4] Cf. Article No. 2 of this series, THIS JOURNAL, 33, 1461–2 (1911).

[5] This point will be discussed in more detail after some investigations now in progress have been brought to a conclusion.

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behavior of the "normal solute" could be ascribed wholly to hydration, this salt must be negatively hydrated. From Table VIII it is clear that the deviation is quite appreciable even at such a low concentration as 0.1 normal. From what has just been said regarding potassium chloride, however, it will be readily understood that in the case of cesium nitrate the hydration is entirely lacking or is too small to compensate for the abnormal behavior referred to above, so that the freezing-point curve is what we might expect for a salt which is unhydrated but which exhibits towards the mass-action law the well known behavior of the strong electrolytes.

Turning finally to lithium chloride, its behavior evidently indicates a comparatively high degree of hydration.

If we consider now the question of the calculation of the degrees of hydration of potassium and lithium chlorides, we meet with numerous difficulties. Evidently deviation from the behavior of the "normal solute" cannot be made the basis for such a calculation because this would give a negative hydration to cesium nitrate. The least objectionable method would probably be to first correct the data for the three salts to the same temperature, 0°, with the aid of heat of dilution data; and then by studying the ions and un-ionized molecules separately, by methods previously indicated,[1] obtain functional relations connecting activity and concentration for each kind of molecules. From these data a curve for the "normal unhydrated strong electrolyte" might perhaps be established, which could be made to serve as the basis for calculating the degree of hydration of another electrolyte which deviated from it. Before such a method can be employed, however, further investigation will be required in order to secure the necessary data. Meanwhile, we can make what may be called the "best guess" in the following manner:

Assume that the cesium nitrate curve of Fig. 2 is the normal curve for an unhydrated uni-univalent salt and assume further that the abnormal behavior which causes the deviation of this curve from that of the "normal solute" affects the other salts to an equal extent. Then if we neglect for the present the differences in temperature and in the degrees of ionization of the salts, the degree of hydration can be calculated from the following equation,

$$N'_{CsNO_3} = \frac{n'(1+\gamma)}{55.53 + n'(1+\gamma) - hn'}, \qquad (9)$$

in which h is the number of moles of water combined with one mole of the salt in question at the concentration n' moles per 1000 grams of water, at which concentration its degree of ionization is γ. N'_{CsNO_3} is the mole fraction of cesium nitrate in a solution which gives the same freezing-point lowering as the salt in question. N'_{CsNO_3} can be obtained graph-

[1] THIS JOURNAL, 32, 492–3 (1910).

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ically from Fig. 3. Such a calculation gives for a 0.5 normal solution, $h =$ about 9 for KCl and about 18 for LiCl, figures whose order of magnitude is doubtless correct.

It is our intention to continue this work until, of the uni-univalent salts, the iodides, nitrates and chlorides of cesium, potassium, sodium and lithium have been included.

10. Cesium Nitrate and the Mass Action Law.

In 1902 W. Biltz published[1] a set of freezing-point data for aqueous solution of cesium nitrate. From these data he calculated, in the usual manner, a set of values for the degree of ionization of the salt in the different solutions studied. On substituting these values in the Ostwald Dilution Law, $\gamma^2/(1-\gamma)V=K$, he found that the values of K thus obtained did not exhibit the usual regular variation with concentration shown by other electrolytes, but showed irregular variations about a mean value of 0.34, throughout the concentration range 0 to 0.43 normal. The values of 100 K which he thus obtained are shown in column VIII of Table IX. From these results Biltz drew the following conclusions: "Das Cäsiumnitrat folgt dem Massenwirkungsgesetze exakt..... Cäsiumnitrat ist demnach der erste starke Elektrolyt, dessen Dissoziationsverhältnisse genau bekannt sind. Dadurch ist zugleich die Annahme widerlegt, dass die Abweichungen von dem Massenwirkungsgesetze durch die Anwesenheit von Ionen in grösserer Zahl prinzipiell bedingt sind. Der Grad der Dissoziation hat, wie man auch schon aus dem zuerst gegebenen Versuchsmaterial ersehen konnte, keinen erkennbaren Einfluss auf der Grösse der Abweichungen, vorausgesetzt, dass man γ aus Gefrierpunktserniedrigungen berechnet."

The results obtained in the present investigation do not confirm the data given by Biltz and the conclusions to which they lead regarding the behavior of this electrolyte with reference to the Law of Mass Action are also somewhat different from those arrived at by Biltz. In view of the frequent citations to the "exceptional" behavior of this salt which one meets in the literature,[2] this question will be considered in the light of the results obtained in our investigation.

Comparison with Biltz's Values.—Column I of Table IX gives the compositions of the solutions investigated by Biltz, column IV contains the corresponding freezing-point lowerings found by him, and column V

[1] *Z. physik. Chem.*, 40, 218 (1902).

[2] *E. g.*, Abegg's "Handbuch der Anorganischen Chemie," Band II (1), p. 450; Weinstein's "Thermodynamik und Kinetik der Körper," Band III (2), p. 716. Morgan's "The Elements of Physical Chemistry," p. 319. Wegscheider in his recent paper, "On the Anomaly of the Strong Electrolytes and the Limits of the Validity of the Dilution Law" (*Z. physik. Chem.*, 69, 627 (1909)), discusses Biltz's results at some length and dissents from the latter's conclusion with respect to the influence of the ions upon the deviation from the Mass Action Law.

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TABLE IX.

No.	I. n'. Mole $CsNO_3$ per 1000 g. water.	II. V_B 17.5°/17.5°. Biltz.	III. V. 0°/4°. W. and M.	IV. Δt_B. Biltz.	V. $\Delta t \pm 0.002°$ W. and M.	VI. $\frac{\Delta t_B}{0.0185n'} - 1 = 100\gamma_B$.	VII. $\frac{\Delta t}{0.0186n'} - 1 = 100\gamma$.	VIII. $\frac{100\gamma_B^2}{(1-\gamma_B)V_B} = 100K_B$.	IX. $\frac{100\gamma^2}{(1-\gamma)V} = 100K$.
1	0.00766	130.7	130.5	0.028	0.028	98.0	96.0 ± 14.0	33	18.0 ± 70.0
2	0.0194	51.6	51.6	0.070	0.068	95.0	88.0 ± 6.0	35	13.0 ± 8.0
3	0.0465	21.6	21.6	0.164	0.157	90.7	81.0 ± 2.0	(41)	16.6 ± 3.0
4	0.0988	10.2	10.17	0.331	0.322	81.0	75.0 ± 1.0	34	22.1 ± 1.6
5	0.1421	7.09	7.09	0.460	0.453	75.0	71.5 ± 0.8	32	25.3 ± 1.2
6	0.2100	4.81	4.81	0.662	0.650	70.4	66.4 ± 0.5	35	27.2 ± 0.8
7	0.2987	3.39	3.40	0.907	0.894	64.1	60.9 ± 0.4	34	27.6 ± 0.6
8	0.3861	2.62	2.64	1.125	1.124	57.5	56.4 ± 0.3	(30)	27.6 ± 0.4
9	0.4339	2.33	2.356	1.267	1.248	57.8	54.6 ± 0.2	34	27.9 ± 0.4
10	(0.5000)	....	2.05	...	(1.419 ± 0.005°)	....	52.6 ± 0.2	..	28.6 ± 0.8

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shows the freezing-point lowerings given by our empirical equation (5). A comparison of the two sets of data shows that from a concentration of 0.05 molal up, all of Biltz's values differ from ours by from 0.01° to 0.02°, except in the case of solution number 8, for which the values are identical.[1]

The Ostwald Dilution Law.—If an electrolyte is assumed to be a *normal solute* and the solution be sufficiently dilute, its degree of ionization would be given by the equation

$$\gamma = \Delta t/k_F n' - 1, \qquad (10)$$

where k_F is molal freezing-point lowering. The theoretical value for k_F as computed from the relation, RT^2_0/L_0 is 1.86° for water. This value is moreover confirmed by the recent careful freezing-point measurements of Bedford,[2] who found for cane sugar solutions the value 1.86° and for potassium chloride solutions the value 3.72° = 2 × 1.86°, at high dilutions.

At the time of Biltz's investigation, 1.85° was the generally accepted value for k_F and he employed this value in calculating the degree of ionization of the cesium nitrate in the solutions investigated by him. His results for 100 γ are shown in column VI of Table IX. If, however, we employ the value 1.86° and use the values for Δt given in column V, we obtain for 100 γ the values shown in column VII. The deviation which would be caused by the probable error in the corresponding value of Δt is also indicated after each value in this column.[3] It is evident that below 0.05 normal the values are too uncertain to be relied upon. Those above 0.3 normal will also be somewhat in error from the fact that equation (10) is applicable only to dilute solutions.

In order to test the mass-action law for cesium nitrate solutions, Biltz substituted the values for γ from column VI and the values for V from column II in the Ostwald Dilution Law,

$$\gamma^2/(1-\gamma)V = K, \qquad (11)$$

and obtained the values for 100 K_B given in column VIII. These values evidently vary irregularly and rejecting Nos. 3 and 8, Biltz adopted 0.34 as the mean value for K.

If the values for γ given in column VII and the values for V of column III be employed, the values for 100 K shown in column IX are obtained. After each value in this column is given the deviation[4] which would be produced by the probable error in the corresponding value of Δt.

[1] Biltz rejected the value for this solution in computing his mean value of K, see column VIII.

[2] *Proc. Roy. Soc. London* (*A*) 83, 454 (1910).

[3] These deviations are computed from the relation $\delta\gamma = \delta(\Delta t)/1.86n'$.

[4] These deviations are computed from the equation

$$\delta K = \left(K + \frac{\Delta t}{0.93} - \frac{2}{V}\right)\frac{\delta(\Delta t)}{3.72n' - \Delta t} \qquad (12)$$

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The values for K are shown graphically in curve IV of Fig. 3. Values of n' are plotted as ordinates and those of K as abscissas, using the scale 1 unit = 0.025 as ordinates and 1 unit = 0.0286 as abscissas. Through each point is drawn a double-headed arrow whose length is equal to the probable error of the location of the point. An inspection of this curve shows that K increases fairly rapidly up to a concentration of about 0.2 normal and from thence up to 0.5 normal it is nearly constant.

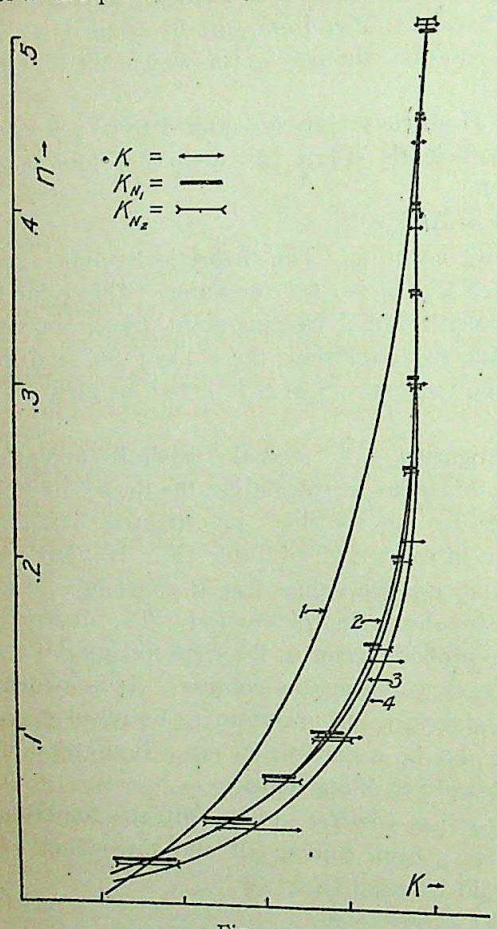

Fig. 3.

Now the Ostwald Dilution Law has no theoretical basis except for very dilute solutions and it is exactly in this region that it is not obeyed by cesium nitrate according to the above calculation. If we wish to study this equilibrium for concentrations above 0.1 normal a more general law for chemical equilibrium should be employed, one which, at least, does not contain the assumption that the solution is dilute.

The Law for Chemical Equilibrium in an Ideal Solution.—The general law for chemical equilibrium is an "ideal" or "perfect" solution and is expressed by the equation[1]

$$\frac{N_A^a \cdot N_B^b \cdots}{N_M^m \cdot N_N^n \cdots} = K_N. \qquad (13)$$

This differs from the Ostwald Dilution Law only in the substitution of *mole fractions* in place of *volume concentrations*. For the dissociation of a binary electrolyte it assumes the form

$$N_i^2/N_U = K_N \qquad (14)$$

where N_i is the mole fraction of each ion and N_U the mole fraction of the un-ionized molecules.

[1] For a derivation of this equation see Contribution No. 1, of this series, THIS JOURNAL, 32, 668 (1910).

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If the solvent is water and the degree of ionization of the salt is γ_N and its concentration is n' moles per 1000 grams of water we have

$$N_i = \frac{\gamma_N n'}{55.53/A + (1 + \gamma_N)n'} \qquad (15)$$

and

$$N_U = \frac{(1 - \gamma_N)n'}{55.53/A + (1 + \gamma_N)n'} \qquad (16)$$

and equation (14) becomes

$$\frac{\gamma_N^2 n'}{[55.53/A + (1 + \gamma_N)n'](1 - \gamma_N)} = K_N \qquad (17)$$

in which A is the association factor for water, *i. e.*, 18 A is the average molecular weight of the water at the temperature in question.

Calculation of γ_N.—In order to calculate γ_N from the freezing-point data, we will make use of the relation connecting the freezing-point lowering and mole fraction of the solute in the case of an "ideal" solution. If water is the solvent and the solution is only moderately concentrated we have seen above (p. 1703), that equation (8) is a sufficiently exact numerical statement of this relation. If we replace N', the mole fraction of the solute, by $\frac{in'}{1000/18 + in'}$ this equation takes the form

$$in' = (\Delta t/1.858)\ (1 + 0.0055\Delta t). \qquad (18)$$

If the electrolyte were a normal solute and were not hydrated, the van't Hoff i or the "mole number" would be equal to $1 + \gamma_N$ and we could therefore employ this equation in order to obtain the degree of ionization of such an electrolyte. Now, as we have seen above, cesium nitrate is probably the least hydrated of all electrolytes and if we apply equation (18) to the data for this salt, we obtain the values for the per cent. of ionization, $100\gamma_N$, which are shown in column II of Table X.

TABLE X.

I. n'.	II. $100\gamma_N$.	III. $100K_N$. $A=2$.	IV. $100K_N$. $A=3$.	V. $100\gamma'$. $\pm 0.3\%$.	VI. $100K'_N \pm 0.1\%$. $A=3$.
0.0250	82.0±4.0	3.4 ±0.8	5.1 ±1.2	89.4	9.2
0.0500	80.0±2.0	5.6 ±0.6	8.4 ±0.9	86.5	13.6
0.0750	77.0±1.0	7.0 ±0.4	10.5 ±0.6	83.8	15.9
0.1000	75.0±1.0	8.4 ±0.4	12.5 ±0.6	81.5	17.6
0.1500	71.3±0.7	9.5 ±0.2	14.3 ±0.3	....	....
0.2000	68.0±0.5	10.2 ±0.18	15.2 ±0.27	75.4	22.8
0.2500	64.8±0.4	10.49±0.14	15.60±0.21	....	....
0.3000	61.7±0.3	10.57±0.10	15.71±0.15	71.9	27.2
0.3500	59.1±0.3	10.63±0.10	15.80±0.15	....	....
0.4000	57.0±0.3	10.67±0.08	15.81±0.12	68.5	29.4
0.4500	55.3±0.2	10.84±0.06	16.08±0.09	....	....
0.5000	(53.6±0.5)	11.1 ±0.26	16.40±0.39	65.8	31.4

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Values of K_N.—We will now substitute these values in equation (17) and calculate the equilibrium constant K_N. Before we can do this, however, it will be necessary to assign some value to the association factor A. This factor is, however, not a constant but is a function of n' and is connected with it in such a way that as n' increases A probably decreases, so that even if we knew the value of A accurately for pure water and employed this value in our equation, we should not expect to find a constant value for K_N even if the Mass Law were obeyed, but a slowly increasing value as the concentration increases. Authorities agree that water at 0° is composed chiefly of double and triple molecules so that A is probably not less than 2 or greater than 3. Two series of values for 100 K_N have therefore been computed, one upon the basis that $A = 2$, column III, and the other upon the basis that $A = 3$, column IV.[1] These values are shown graphically in curves II and III, respectively, in Fig. 3, values of n' being plotted as ordinates and values of 100 K_N as abscissas using the scale, 1 unit = 0.025 as ordinates and 1 unit = 0.0111 and 0.0164, respectively, as abscissas.

An inspection of these curves shows that between 0.2 and 0.5 normal 100 K_N increases slowly (from 10.2 to 11.1 for $A = 2$ and from 15.2 to 16.4 for $A = 3$). The direction of the curve in the more dilute solutions, however, indicates that at high dilutions K_N must have a very different value.

The Equilibrium "Constant" Computed from Conductivity Data.—By employing the equation $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^{0.826}$ for calculating the degree of ionization we obtained the values for γ given in column V of Table X. It will be noted that they are uniformly larger than those obtained from the freezing-point data.

If these values be substituted in equation (17), the values for the equilibrium constant, K'_N, given in column VI of Table X, are obtained. These are shown graphically in curve I of Fig. 3. As in the other curves of this figure, the scale for the abscissa was 1 unit = 0.1 of the value of K'_N for $n' = 0.5$. The values of K'_N increase continuously with n' which is the normal behavior for a strong electrolyte.

Conclusion.—The characters of the curves shown in Fig. 3 are in general the same. Curve I, however, shows a fairly gradual rise of K throughout its whole course, while the other curves show a rapid rise at first, followed by a very slow rise, so slow in fact that it is perhaps within the experimental error. There is, however, some indication that from 0.4 normal on, a more rapid rise again occurs in the case of curves II and III. Although between 0.2 and 0.4 normal K_N appears to be reasonably con-

[1] The probable errors given for these values of K are computed from the relation

$$\partial K_N = [K_N + 0.0192A\ \Delta t - 0.036A\ n'] \frac{0.54\partial(\Delta t)}{2n' - 0.54\Delta t}. \qquad (19)$$

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stant, the remainder of the curve (II or III) clearly will not justify the statement that the mass-action law is obeyed by this salt when γ is obtained from freezing-point data. With cesium nitrate, therefore, as with the other strong electrolytes, the freezing point method cannot be relied upon to give correct values for γ, for the validity of the mass-action law is implicitly assumed whenever γ is calculated by this method.

11. Summary.

1. The freezing point lowerings, densities, relative viscosities, and equivalent conductances of solutions of cesium nitrate, potassium chloride, and lithium chloride at 0° have been investigated and a complete set of these data are given in Tables V, VI, and VII. The data extend to normal solutions in the case of potassium and lithium chlorides and to 0.5 normal in the case of cesium nitrate.

2. The cryohydric point for cesium nitrate is —1.254°.

3. When the freezing-point curves (Fig. 2, mole fraction of solute plotted against freezing-point lowering) for the three salts are compared with the curve of the "normal solute," potassium chloride is found to agree exactly up to about 0.5 normal, lithium chloride deviates decidedly in the direction of hydration while cesium nitrate deviates decidedly in the opposit direction. The conclusion is drawn that deviation from the behavior of a "normal solute" (an unhydrated non-electrolyte) cannot serve as a basis for the calculation of the degree of hydration of an electrolyte. Another method for making this calculation is outlined and, as a provisional result, about 9 molecules of water are found to be in combination with one of KCl and about 18 with one of LiCl in a half normal solution of the electrolyte.

4. The freezing-point data for cesium nitrate are compared with the data of Biltz and his conclusion, that this salt obeys the Mass Action Law, is only partially substantiated.

URBANA, ILL.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 199.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. X. THE DROP WEIGHTS OF SOME FURTHER ASSOCIATED AND NON-ASSOCIATED LIQUIDS, AND THE SURFACE TENSIONS AND CAPILLARY CONSTANTS CALCULATED FROM THEM.

BY J. LIVINGSTON, R. MORGAN AND F. T. OWEN.

Received September 19, 1911.

The associated and non-associated liquids used in this research were selected for the following purposes: (1) The further testing of the new

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definition of normal molecular weight in the liquid state;[1] (2) the further comparison of the surface tension and capillary-constant values calculated from the results of the Morgan drop weight apparatus[2] with those found by other observers from measurements of capillary rise; and (3) to supply additional data for a later quantitative study of the relationship existing between the drop weight, or the values derived from it, and the other physical and chemical properties of the liquid.

For convenience, and to avoid unnecessary loss of time in case of accident, two pieces of apparatus, with tips of different diameters, were employed, but it was not necessary in any case to complete the study of any liquid on one tip after having started it with the other. If an accident had happened, however, this would have been possible, as has already been brought out in a previous paper,[3] and just as it is possible to calculate values of t_c, or of the surface tension, or the capillary constant, from the results on one tip, which would be identical (within the limits of error) with those obtained by a similar calculation from the results with the same liquid at the same temperature on another tip. Thus for the same liquid, at the same temperature (t_o) we would have for the two tips the relationships

$$w'(\mathrm{M}/d)^{\frac{2}{3}} = k'_{\mathrm{B}}(t_c - t_o - 6)$$

and

$$w''(\mathrm{M}/d)^{\frac{2}{3}} = k''_{\mathrm{B}}(t_c - t_o - 6),$$

from which it is evident, since at the same temperature for the same liquid, M, d, t_c, and t_o are identical in the two equations, that

$$w' : w'' :: k'_{\mathrm{B}} : k''_{\mathrm{B}},$$

the weight of a drop of liquid from one tip is related to that of the same liquid, at the same temperature, from another tip, as are the k_{B} values of the two tips.

By similar reasoning it can be shown that the k_{B} values themselves of the two tips are related as the respective drop weights of benzene falling from them at the same temperature of observation (t_o), for then we would have

$$w'_{\mathrm{B}}(78/d)^{\frac{2}{3}} = k'_{\mathrm{B}}(288.5 - t_o - 6)$$

and

$$w''_{\mathrm{B}}(78/d)^{\frac{2}{3}} = k''_{\mathrm{B}}(288.5 - t_o - 6)$$

which would reduce to

$$w'_{\mathrm{B}} : w''_{\mathrm{B}} :: k'_{\mathrm{B}} : k''_{\mathrm{B}}.$$

[1] Morgan, THIS JOURNAL, 33, 643–657 (1911). *The molecular weight of a liquid is to be regarded as normal (i. e., is identical with that as a gas) when t_c in the equation $w(\mathrm{M}/d)^{\frac{2}{3}} = k_{\mathrm{B}}(t_c - t_o - 6)$ is found to be constant at all temperatures of observation (t_o), k_{B} being the value found for benzene on the same tip, when t_c is taken as equal to the observed critical temperature, viz., 288°.5.*

[2] THIS JOURNAL, 33, 349–362 (1911).

[3] Morgan and Cann, THIS JOURNAL, 33, 1060–1071 (1911).

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And in the same way the surface tension values can be calculated from the drop weight, for then we would have, *for the same liquid at the same temperature,*

$$\gamma(M/d)^{\frac{2}{3}} = K_B(t_c - t_o - 6)$$

and

$$w(M/d)^{\frac{2}{3}} = k_B(t_c - t_o - 6),$$

where M, d, t_c and t_o are the same and consequently

$$\gamma : w :: K_B : k_B$$

i. e.,

$$\gamma = w \times K_B/k_B,$$

γ in dynes and w in milligrams, being values at identical temperatures.

Here again $K_B : k_B :: \gamma_B : w_B$, where γ_B and w_B are the respective values for benzene at the same temperature of observation (t_o), for

$$\gamma_B(78/d)^{\frac{2}{3}} = K_B(288.5 - t_o - 6)$$

and

$$w_B(78/d)^{\frac{2}{3}} = k_B(288.5 - t_o - 6),$$

the values of t_o and d being identical, so that

$$\gamma_B : w_B :: K_B : k_B.$$

Since no general relationship like the above holds for the capillary constant, a^2, the relationship between the drop volume (*i. e.*, drop weight at t_o/density at t_o) and the capillary constant can be found only by a direct comparison of individual results at various temperatures, and then finding the mean of the constant by which the drop volume must be multiplied to give the observed capillary constant. In a previous paper[1] it was shown that for a tip giving a value of $k_B = 2.3502$, a^2 (= height of ascension, times radius of bore) for benzene as found at a number of temperatures by four of the best modern workers with the capillary rise method can be obtained from the drop weight from that tip by aid of the equation

$$a_t^2 = 0.1837\, w_t'/d_t,$$

so that for any new tip, since the drop weight is proportional to the normal (benzene) constant of the tip, for

$$w_t' : w_t'' :: k_B' : k_B'',$$

i. e.,

$$w_t' = k_B'/k_B' w_t'',$$

we have for *any* liquid from *any* tip

$$a_t^2 = 0.1837 \times 2.3502/k_B'' \times w_t''/d_t$$

where k_B'' and w_t'' are the values for the new tip.

The benzene values for the two tips employed in this research are given in the table below, the mean value of w from several determinations

[1] Morgan and McAfee, THIS JOURNAL, 33, 1275–1290 (1911).

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(which varied among themselves as slightly as those given in the previous papers) being the one used.[1]

CALIBRATION WITH BENZENE. M = 78; t_c = 288.5.

t.	d.	w.	$w(M/d)^{\frac{2}{3}}$.	$k_B = \frac{w(M/d)^{\frac{2}{3}}}{288.5-t_0-6}$.
		Tip No. 1.		
39.3	0.86792	30.088	603.68	2.3936
		Tip No. 2.		
30.1	0.86792	29.058	582.87	2.3098

To obtain the surface tension in dynes per centimeter from the drop weights then, we have the equations

I. $$\gamma = w_1 \times \frac{2.1148}{2.3936} = 0.88352 \times w_1; \qquad \textit{Tip No. I.}$$

II. $$\gamma = w_2 \times \frac{2.1148}{2.3098} = 0.91558 \times w_2; \qquad \textit{Tip No. II.}$$

where 2.1148 is the average value of K_B for the surface tension of benzene from capillary rise, using t_c = 288.5° and calculated from the work of the four best modern investigators.[2]

And to calculate the values of the capillary constant, as mentioned above, we have then only to make use of the equations:

III. $$a^2 = 0.1837 \frac{2.3502}{2.3936} \times w_1/d = 0.18037 \times w_1/d. \quad \textit{Tip No. I.}$$

IV. $$a^2 = 0.1837 \frac{2.3502}{2.3098} \times w_2/d = 0.18691 \times w_2/d. \quad \textit{Tip No II.}$$

From the k_B values of the two tips given above we can also, of course, calculate the mean diameters of the tips, for in a previous paper[3] it was shown that

$$\text{diameter} = (k_B/0.4224) \text{ mm.}$$

According to this relationship the diameter of tip No. I was 5.643 mm., while that of tip No. II was 5.445 mm.

In the following tables are given the results obtained with the 12 (7 non-associated, 5 associated) liquids studied, together with the calculated values of t_c, surface tension, and capillary constant, and, wherever it is possible, the similar values observed by other investigators.

Methyl Hexyl Ketone, $CH_3COC_6.H_{13}$; M = 128.13.

Kahlbaum's preparation, redistilled, density at 0° extrapolated, and that at 30.1° interpolated, from the results by Falk[4] on the same sample. *Tip No. I.*

[1] In order to save space the mean only of the drop weight at the various temperatures is also given for the other liquids studied.

[2] Morgan and McAfee, *Loc. cit.*, 1280.

[3] Morgan and Cann, *Loc. cit.*

[4] THIS JOURNAL, 31, 86 and 806.

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t.	d.	w.	$w(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.3936$.
0	0.8362	31.324	896.96	380.7
30.1	0.8106	28.202	824.47	380.5

It is evident that this liquid is perfectly normal and non-associated, the values of t_c agreeing (0.05 per cent.) within the experimental error. Assuming a linear relationship between the drop weight and the temperature, and also between the drop volume and temperature, we find

$$w_t = 31.324 - 0.10372t,$$

and

$$v_t = w_t/d_t = 37.460 - 0.08864t,$$

from which it follows, by aid of equations I and III respectively, that

$$\gamma_t = 27.675 - 0.09164t$$

and

$$a_t^2 = 6.757 - 0.016t.$$

Benzyl Cyanide, $C_6H_5CH_2CN$; M = 117.1.

Kahlbaum's preparation, redistilled. Densities interpolated from Falk's[1] observations on this sample. *Tip No. I.*

t.	d.	w.	$w(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.3936$.
45	0.9981	42.654	1022.20	478.1
60	0.9850	40.772	985.77	477.8

This compound, according to the new definition of normal molecular weight, is non-associated, the deviation in the value of t_c being less that 0.1 per cent. Assuming linear relationships, we have

$$w_t = 48.302 - 0.1255t$$

and

$$v_t = 46.763 - 0.0895t,$$

from which by aid of I and III we find

$$\gamma_t = 42.676 - 0.1109t$$

and

$$a_t^2 = 8.435 - 0.01614t.$$

Benzaldehyde, C_6H_5CHO; M = 106.05.

Preparation of Kahlbaum's, redistilled. Densities from Kopp.[2] *Tip No. I.*

30.2	1.0349	42.358	927.56	423.7
50.0	1.0169	39.914	884.33	425.5

At 20° Landolt finds a density of 1.0473 (his only value) as compared to 1.0442 of Kopp, which would leave some doubt as to the accuracy of Kopp's figures. The value of w at 50° here was determined immediately after the distillation, while that at 30.2° was not found until the following day. Considering these two facts, especially in view of the

[1] *Loc. cit.*

[2] Liebig's *Ann.*, 94, 316 (1855).

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known instability of this substance, it is more than probable that the liquid is normal and non-associated, for the above discrepancy in the values of t_c of 1.8°, *i. e.*, of 0.42 per cent. can readily be ascribed to them.

From capillary rise Ramsay and Shields find for this liquid:

t.	d.	r.	$r(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.1012$.
15°.4	1.0480	39.19	850.6	426.3
78.3	0.9915	31.72	714.4	424.3

Regarding the temperature change of drop weight, as well as drop volume, as linear we find

$$w_t = 46.084 - 0.1234t$$

and

$$v_t = 43.491 - 0.0848t,$$

the application of I and III giving

$$\gamma_t = 40.716 - 0.109t$$

and

$$a_t^2 = 7.844 - 0.0153t.$$

Interpolating between the values of Ramsay and Shields, we find for γ and a^2 the following values compared with those from the above equation:

t.	γ M & O.	γ R & S.	a^2 M & O.	a^2 R & S.
30.2	37.424	37.43	7.382	7.360
50.0	35.266	35.09	7.079	7.014

Piperidine, $CH_2(CH_2CH_2)NH$; M = 85.08.

Kahlbaum preparation, redistilled. *Tip No. I.* Above 30° the liquid in the apparatus turned yellow, so that no determinations above that point were attempted. The densities here were taken from the formula

$$d_t = 0.88125 - 0.000991t$$

obtained as a mean of the equations found from the densities employed by Ramsay and Shields and by Ramsay and Aston, *viz.*: $0.88025 - 0.000995t$, and $0.8822 - 0.000987t$, for it seems to agree better in general with the results obtained by others than do theirs; thus at 0° Ladenburg and Roth[1] find 0.8810. The values calculated for t_c here are

t.	d.	w.	$w(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.3936$.
0	0.88125	35.720	751.73	320.1
30	0.85152	31.648	681.45	320.7

from which it is evident that the liquid is perfectly normal in its behavior, and non-associated.

The values of t_c, as well as those quantities from which that is derived, as found by Ramsay and Shields and by Ramsay and Aston, are given in the following tables:

[1] *Ber.*, 17, 513.

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Ramsay and Shields, $k_B = 2.1012$.

16.5	0.8640	29.89	637.1	325.7
46.4	0.8337	26.43	576.8	326.9
78.4	0.8024	22.75	509.3	326.8

Ramsay and Aston, $k_B = 2.1212$.

15.2	0.8670	29.67	635.6	320.9
46.2	0.8363	26.21	570.7	321.7
78.4	0.8048	22.46	501.8	321.0
132.5	0.7256	16.72	390.6	322.6

Assuming the relationships to be linear we find for drop weight and for drop volume from this tip the equations

$$w_t = 35.720 - 0.1357t$$

and

$$v_t = 40.534 - 0.1122t,$$

from which it follows from I and III that

$$\gamma_t = 31.559 - 0.1199t$$

and

$$a_t^2 = 7.311 - 0.02024t;$$

while from 16.5° to 46.4° Ramsay and Shields find $\gamma_t = 31.79 - 0.1155t$ and Ramsay and Aston $\gamma_t = 31.35 - 0.11t$; and $a_t^2 = 7.392 - 0.0205t$ and $a_t^2 = 7.260 - 0.0187t$, respectively.

From these relationships we find at 0° and 30° the various values of γ and a^2 to be:

	γM & O.	γR & S.	γR & A.	a^2M & O.	a^2R & S.	a^2R & A.
0	31.559	31.79	31.36	7.311	7.392	7.260
30	27.962	28.32	28.03	6.704	6.777	6.700

Diisoamyl, $((CH_3)_2CHCH_2CH_2)_2$; M = 142.18; t_c obs. = 402°.

Kahlbaum preparation, redistilled. Density at 0° from Wurtz;[1] that at the others interpolated from the results of Falk on this same sample. With *Tip No. I* the following results were obtained:

t.	d.	w.	$w(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.3936$.
0	0.7413	26.114	868.50	368.3
30	0.7161	23.344	794.48	368.0

It is evident that this liquid, also, is non-associated.

The variation with temperature of the drop weight, assuming it to be linear, is

$$w_t = 26.114 - 0.09203t$$

and that of the drop volume is

$$v_t = 35.227 - 0.0873t$$

which by aid of I and III lead to

$$\gamma_t = 23.072 - 0.08131t$$

and

[1] *Jahresber. Fortschritte d. Chem.*, 8, 573.

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$$a^2 = 6.354 - 0.01575t.$$

The only measurements of the capillary rise of this liquid are those by Schiff which lead to the quite different values $a^2_{2.6} = 6.603$ and $a^2_{189.1} = 3.579$ as compared to 6.313 and 3.848 (the latter extrapolated through 129°) from the above formula.

Isoamyl Acetate, $C_2H_3O_2C_5H_{11}$; M = 130.11.

Kahlbaum preparation, redistilled. Densities from Bolle and Guye.[1] *Tip No. II.*

t.	d.	w.	$w(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.3098$.
0	0.8941	28.076	776.80	342.4
49.7	0.8444	23.032	662.01	342.4

This liquid, according to the definition, is perfectly normal and non-associated. From the above values, assuming linear relationships, we find

$$w_t = 28.076 - 0.1015t,$$

and

$$v_t = 31.401 - 0.0830t,$$

from which it follows, employing II and IV, that

$$\gamma_t = 25.706 - 0.09293t$$

and

$$a^2_t = 5.869 - 0.01551t.$$

No results of capillary rise are to be found in the literature.

Nitrobenzene, $C_6H_5NO_2$; M = 123.05.

Kahlbaum preparation, redistilled. Densities from Guye and Baud,[2] $d_t = 1.3057 - 0.000845(t-11) - 0.00000125(t-11)^2$. *Tip No. II.*

t.	d.	w.	$w(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.3098$.
30.2	1.1908	44.950	989.82	464.8
49.7	1.1729	42.592	947.42	466.0

From capillary rise the following results have been obtained:

Guye and Baud, $k_B = 2.1012$.

t.	d.	γ.	$\gamma(M/d)^{\frac{2}{3}}$.	t_c.
9.4	1.2090	43.80	954.5	465.4
55.5	1.1680	38.41	856.5	469.2
98.8	1.1240	33.26	760.9	467.0
153.0	1.0625	27.40	650.8	469.0

Ramsay and Shields, $k_B = 2.1012$.

13.6	1.188	42.75	942.8	468.3
78.4	1.124	34.89	798.2	464.3
156.2	1.047	26.94	646.0	469.7

Owing to the varying values found by various observers for the density of this liquid, the results from drop weight may be taken as showing that

[1] *J. chim. phys.*, 3, 39 (1905).

[2] *Arch. sci. phys. et nat. Geneva*, [4] 11, 466 (1901).

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it is non-associated notwithstanding the discrepancy of 1.2° in t_c. The values of w_t and v_t found above, assuming linear relationships, lead to the equations

$$w_t = 48.601 - 0.1209t$$

and

$$v_t = 39.970 - 0.07359t$$

from which by II and IV we obtain

$$\gamma_t = 44.498 - 0.1107t$$

and

$$a_t^2 = 7.471 - 0.01376t.$$

Walden[1] expresses the results of Guye and Baud by means of the equations

$$\gamma_t = 44.945 - 0.1178t$$

and

$$a_t^2 = 7.533 - 0.01492t.$$

A comparison of the values from these equations at the temperatures 30.2° and 49,7° with the values from the equations from drop weight as well as those interpolated from Ramsay and Shields is made in the following table:

Values of a^2 and of γ.

t.	a^2M & O.	a^3W.	a^2R & S.	γM & O.	γW.	γR & S.
30.2	7.055	7.072	7.080	41.155	41.387	40.74
49.7	6.787	6.791	6.776	38.996	39.090	37.38

The striking thing about these results is that while the Ramsay and Shields values differ widely for γ, they are in good agreement with the others as far as concerns a^2. This, of course, is due to the fact that Ramsay and Shields used the quite different densities of Kopp, which affect the results $\gamma = {}^1/_2 \times h \times d \times r$, while the a^2 values are simply the product of the height and the radius. The values of γ calculated from the drop weight are of course independent of the density, while those for a^2 are calculated with a knowledge of that factor.

Methyl Ethyl Ketone, $CH_3COC_2H_5$; M = 72.06.

Sample from Eimer and Amend, prepared by Emerson. Densities from the volumes of Thorpe and Jones.[2] The drop weights from *Tip No. II*, together with those calculated from the equation found from them by the method of least squares, are given below:

$$w_t = 28.358 - 0.1279t + 0.000199t^2.$$

t.	w (obs.).	w (from equation).	Δ.
0	28.353	28.358	+0.005
15	26.514	26.484	—0.030
30	24.664	24.700	+0.036
45	23.020	23.005	—0.015

[1] *Z. physik. Chem.*, 65, 142 (1908).
[2] *J. Chem. Soc.*, 63, 283 (1893).

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while the drop volumes are

$$v_t = 34.190 - 0.11434t + 0.0001709t^2.$$

t.	w/d.	v (from equation).	Δ.
0	34.176	34.190	+0.014
15	32.553	32.513	—0.040
30	30.874	30.914	+0.040
45	29.404	29.391	—0.013

The application of the new definition of normal molecular weight leads to the following values of t_c:

t.	d.	w.	$w(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.3098$.
0	0.82961	28.353	556.09	246.8
15	0.81449	26.514	526.47	249.0
30	0.79886	24.664	496.13	250.8
45	0.78288	23.020	469.28	254.2

from which it is evident that the liquid is abnormal, *i. e.*, associated.

No values from capillary rise are to be found in the literature but the application of II and IV to the drop weight and drop volume equations lead to

$$\gamma_t = 25.964 - 0.1171t + 0.0001822t^2$$

and

$$a_t^2 = 6.391 - 0.02137t + 0.00003194t^2.$$

Diethyl Ketone, $C_2H_5COC_2H_5$; M = 86.08.

Sample obtained through Eimer and Amend from Emerson, redistilled within 0.1°. Densities calculated from the volumes given by Thorpe and Jones.[1] The observed drop weights from *Tip No. I*, as well as those calculated from the equation derived from them, are as follows:

$$w_t = 29.394 - 0.1133t.$$

t.	w (obs.).	w (from equation).	Δ.
0	29.404	29.394	—0.010
15	27.696	27.694	—0.002
30.1	25.958	25.984	+0.026
45	24.310	24.295	+0.015

while for drop volumes we have

$$v_t = 25.253 - 0.10634t - 0.0001787t^2.$$

t.	w/d (obs.).	v (from equation).	Δ.
0	35.278	35.253	—0.025
15	33.618	33.698	+0.080
30.1	32.300	32.214	—0.086
45	28.800	28.830	+0.030

The application of the definition of normal molecular weight leads to the following values of t_c:

[1] *Loc. cit.*

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t.	d.	w.	$w(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.3936$.
0	0.83350	29.404	647.25	276.4
15	0.82384	27.696	618.11	278.7
30.1	0.80365	25.958	585.46	280.7
45	0.78929	24.310	554.92	282.8

from which it is clear that the liquid is abnormal, *i. e.*, associated. The use of I and III leads here with the equations for w_t and v_t to.

$$\gamma_t = 25.970 - 0.1001t$$

$$a_t^2 = 6.363 - 0.01919t + 0.00003225t^2$$

but no values from capillary rise are to be found in the literature.

Propyl Alcohol, C_3H_7OH; M = 60.06.

Kahlbaum preparation, redistilled. Densities are from Young.[1] The drop weights found and calculated from an equation are as follows: *Tip No. I.*

$$w_t = 27.817 - 0.08857t.$$

	w (obs.).	w (from equation).	Δ.
—5.7	28.362	28.322	—0.040
+0.2	27.740	27.799	+0.059
7.1	27.188	27.188	0.000
22.4	25.872	25.833	—0.039
34.5	24.744	24.761	+0.017
58.2	22.636	22.662	+0.026
70.2	21.620	21.599	—0.021

The drop volumes (w_t/d_t) given below are at temperatures at which Young gives values for the density, the values of w being those from the above equation.

$$v_t = 33.950 - 0.07586t - 0.0000502t_8.$$

t.	d.	w.	w/d.	v (from equation).	Δ.
0	0.8193	27.817	33.952	33.950	—0.002
20	0.8035	26.046	32.416	32.413	—0.003
40	0.7875	24.274	30.824	30.836	+0.012
60	0.7700	22.503	29.225	29.217	—0.008

That propyl alcohol is abnormal in molecular weight, *i. e.*, is associated, is shown by the following values of t_c (a fact which is also confirmed by results from capillary rise):

t.	d.	w.	$w(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.3936$.
0	0.8193	27.817	487.24	209.6
20	0.8035	26.046	462.18	219.1
40	0.7875	24.274	436.55	228.4
60	0.7700	22.503	410.81	237.6

From the above equations for w and v, we find, by aid of I and III, the following values for γ and a^2:

[1] *Proc. Roy. Soc. Dub.*, **12** (N. S.), 442 (1910).

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$$\gamma_t = 24.577 - 0.07825t$$

and

$$a_t^2 = 6.124 - 0.01368t - 0.00000906t^2.$$

A comparison of the values of γ and a^2 found from these equations with those found by other observers (Renard and Guye, Ramsay and Shields) by the method of capillary rise is made in the two tables below, at the temperatures at which they worked. All numbers which are in parentheses are found by interpolating or extrapolating, using the temperature coefficient found from the two nearest figures; this is also true with all the other tables given later.

Values of γ.

t.	M & O (from equation).	R & G.	R & S.
10.2	23.778	*23.69*	(24.34)
16.4	23.294	(23.19)	*23.82*
36.0	21.760	*21.61*	(22.15)
44.5	21.095	*21.05*	(21.41)
46.3	20.954	(20.90)	*21.29*
57.8	20.054	*19.97*	(20.35)
65.9	19.420	*19.27*	(19.68)
75.8	18.646[1]	*18.33*	(18.87)
78.3	18.450[1]	(18.19)	*18.67*
90.6	17.488[1]	*17.48*	(17.66)

Values of a^2.

t.	M & O.	R & G.	R & S.
5.8	6.044	(6.007)	(6.181) Schiff *6.223*
10.2	5.984	*5.943*	(6.112)
16.4	5.897	(5.852)	*6.014*
36.0	5.620	*5.565*	(5.704)
44.5	5.497	*5.468*	(5.570)
46.3	5.465	(5.441)	*5.543*
57.8	5.303	*5.268*	(5.364)
65.9	5.183	*5.132*	(5.237)
75.8	5.035[1]	*4.934*	(5.083)
78.3	4.997[1]	(4.916)	*5.045*
90.6	4.810[1]	*4.771*	(4.853)
97.1	4.710[1]	(4.699)[1]	(4.752) Schiff *4.718*

As will be observed from the above the values from drop weight always lie between those found by Renard and Guye and those of Ramsay and Shields, more closely approaching, however, those of the former.

Propionitrile, C_2H_5CN; M = 55.04.

Kahlbaum preparation, redistilled. Densities from Thorpe.[2]

$$d_t\ 0.80101 - 0.0009815t - 0.000000125t^2. \quad \textit{Tip No. I.}$$

[1] Extrapolated.

[2] *Trans. Chem. Soc.*, 37, 141 and 327.

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$$w_t = 31.942 - 0.11657t.$$

t.	w (obs.).	w (from equation).	Δ.
6.5	31.190	31.185	—0.005
17.7	29.859	29.879	+0.020
37.7	27.560	27.547	—0.013
60.3	24.950	24.913	—0.037
71.2	23.608	23.642	+0.034

$$v_t = 39.840 - 0.09066t - 0.0002045t^2.$$

	d (Thorpe).	w (from equation).	w/d.	v (from equation).	Δ.
0	0.80101	31.942	39.877	39.840	—0.037
20	0.78117	29.611	37.906	37.945	+0.039
40	0.76093	27.279	35.850	35.886	+0.036
60	0.74027	24.948	33.701	32.664	—0.037

That this liquid, also, is abnormal, *i. e.*, associated according to the new definition, is shown by the following t_c values at the above even temperatures.

t.	$w(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.4936$.	
0	535.87	229.9	At 16.8° R. and S. find 238.7°
20	515.14	237.0	
40	473.57	243.9	
60	441.13	250.3	At 61.8° R. and G. find 249.7°

From the equations for drop weight and drop volume, we find, using I and III,

$$\gamma_t = 28.221 - 0.103t$$
$$a_t^2 = 7.186 - 0.01635t - 0.00003689t^2.$$

In the table below the values of γ and a^2 as found by aid of these equations are compared with those found at other temperatures by the capillary rise method.

	Values of γ.				Values of a^2.		
t.	M & O.	R & S.	R & G.	t.	M & O.	R & S.	R & G.
11.8	27.006	(27.21)	*27.29*	11.8	6.988	(7.030)	*7.038*
16.8	26.491	*26.68*	(26.74)	16.8	6.901	*6.933*	(6.913)
31.3	24.997	(25.14)	*25.13*	31.3	6.638	(6.652)	*6.652*
46.4	23.442	*23.55*	(23.39)	46.4	6.348	*6.358*	(6.329)
48.1	23.267	(23.36)	*23.19*	61.8	6.035	(6.018)	*6.000*
61.8	21.856	(21.91)	*21.69*	78.1	5.685[1]	(5.657)	*5.631*
78.1	20.177[1]	(20.18)	*19.92*	78.3	5.681[1]	*5.653*	(5.627)
78.3	20.156[1]	*20.18*	(19.90)	89.9	5.417[1]	(5.397)	*5.382*
89.9	18.961[1]	(18.93)	*18.67*	97.0	5.253[1]	(5.240)	(5.232) Schiff *5.453*

Acetone, CH_3COCH_3; M = 58.05.

Kahlbaum preparation, redistilled. Densities from Thorpe's volumes. *Tip No. II.*

$$w_t = 27.666 - 0.1339t.$$

t.	w (obs.).	w (from equation).	Δ.
15	25.674	25.657	—0.017
30.1	23.610	23.636	+0.026
60	19.642	19.632	—0.010

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$$v_t = 33.993 - 0.1296t.$$

t.	d.	(w obs./d).	v (from equation).	Δ.
15	0.80177	32.022	32.049	+0.027
30.1	0.78348	30.135	30.092	—0.043
60	0.74962	26.203	26.217	+0.014

The values of t_c calculated for this liquid show it, also, to be abnormal, *i. e., associated.*

t.	$w(M/d)^{\frac{2}{3}}$.	t_c from $k_B = 2.3098$.
15	445.99	214.1
30.1	416.50	216.5
60	356.86	220.5

From the above weight and volume relations, by aid of II and IV, we obtain

$$\gamma_t = 25.330 - 0.1226t$$

and

$$a_t^2 = 6.354 - 0.02422t.$$

The values of γ and a^2 observed by the various investigators (Ramsay and Shields, Dutoit and Friederich, and Renard and Guye), or interpolated or extrapolated from their work, are compared with those calculated from the above equations in the following tables:

Values of γ.

t.	M & O.	R & S.	D & F.	R & G.
—1.2	25.477[1]	(25.58)	*25.76*	(25.41)
12.9	23.748[1]	(23.83)	(24.00)	*23.96*
16.8	23.271	*23.35*	(23.61)	(23.56)
21.0	22.755	(22.83)	(22.98)	*23.13*
21.8	22.657	(22.73)	*22.89*	(23.02)
30.0	21.652	(21.71)	(21.62)	*21.93*
33.8	21.186	(21.24)	*21.03*	(21.50)
44.1	19.923	(19.96)	(19.92)	*20.33*
46.4	19.641	*19.68*	(19.67)	(20.09)
55.1	18.575	(18.64)	(18.72)	*19.19*
56.6	18.513	(18.59)	*18.67*	(19.14)
78.3	15.730[1]	*15.90*	(16.22)	(16.78)

Values of a^2.

1.2	6.383[1]	(6.380)	*6.410*	(6.324)
12.9	6.042[1]	(6.052)	(6.038)	*6.074*
16.8	5.974	*5.958*	(5.935)	(6.005)
21.0	5.845	(5.857)	(5.824)	*5.931*
21.8	5.826	(5.838)	*5.802*	(5.910)
30.0	5.627	(5.641)	(5.617)	*5.693*
33.8	5.535	(5.550)	*5.532*	(5.608)
44.1	5.286	(5.303)	(5.292)	*5.378*
46.4	5.230	*5.246*	(5.238)	(5.332)
55.1	5.019	(5.029)	(5.037)	*5.159*
55.6	5.007	(5.016)	*5.025*	(5.149)
78.3	4.458[1]	*4.456*	4.496	(4.695)

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Just as with nitrobenzene, the agreement in the a^2 values here is better than that of the γ values. It must be remembered again in this connection that the surface tensions from capillary rise are dependent upon the density, and the various observers have not all used the same values while the γ value from drop weight is independent of density, except that of benzene, for it is from the γ values of that only that the constant for the transformation of w into γ is found. The a^2 values, on the other hand, are dependent, when found from drop weight, upon the density, while those from capillary rise are directly observed. The better agreement of the a^2 values, then, is a proof that the densities we have employed (Thorpe's) are the correct ones, for they transform directly observed drop weight results into indirect values agreeing with the directly observed capillary rise, or would transform directly observed capillary rise values into calculated surface tensions agreeing with those found directly from directly observed drop weights.

Summary.

I. On the basis of the new definition of normal molecular weight in the liquid state, the finding of a calculated value of t_c independent of the temperature of observation (t_o) in the equation $w(M/d)^{\frac{2}{3}} = k_B(t_c - t_o - 6)$, where k_B is found from the same equation for *benzene* at all temperatures when its observed critical point, 288.5°, is used as t_c, it is shown that methyl hexyl ketone, benzyl cyanide, benzaldehyde, piperidine, diisoamyl, isoamyl acetate, and nitrobenzene are perfectly normal, *i. e.*, non-associated, the calculated t_c remaining constant within the limits of error. Methyl ethyl ketone, diethyl ketone, propyl alcohol, propionitrile, and acetone on the other hand are abnormal, *i. e.*, associated, for the values of t_c calculated for them increase with increased temperature of observation.

II. The values of surface tension in dynes, γ, and of the capillary constant a^2, calculated respectively from the drop weights and the drop volumes, are found to agree with the values observed from capillary rise even better than these do when found by different observers, for in most cases where comparison is possible, the values from the drop weight method lie between those found by the investigators on capillary rise.

III. Equations giving the variation of the surface tension γ and the capillary const. a^2, as found from the drop weight, are given for all the above liquids, that for γ being especially important for it is independent of any knowledge of the density of the liquid, a cause of variation, all too often encountered in the results by the capillary rise method. The values of a^2, on the other hand, are here dependent upon the density, but as great care has been taken in the selection of the observed values, those of Thorpe or Young being used when possible, it is thought that great stress may also be laid upon them.

LABORATORY OF PHYSICAL CHEMISTRY.

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BEHAVIOR OF THE HYDRONITROGENS AND THEIR DERIVATIVES IN LIQUID AMMONIA. I. AMMONOLYSIS OF HYDRAZINE SULFATE.

By A. W. Browne and T. W. B. Welsh.

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In 1899 Goldschmidt and Salcher[1] studied the distribution of hydrochloric, hydrobromic, nitric, and orthobenzoic acids between certain tertiary bases and aniline, which was used as the solvent. The process by which these bases were to a certain extent liberated from their salts by the action of the solvent was designated by the authors, in recognition of a certain analogy with hydrolysis, as *aminolysis*.

In 1905 Franklin[2] brought to light the remarkable analogy that exists between the reactions involved in ordinary hydrolysis and the reactions in which ammonia effects the decomposition of various substances with formation of amides, imides, nitrides, or ammono-basic salts. In accordance with this analogy the breaking up of certain substances by the action of ammonia was appropriately regarded as a process of *ammonolysis*.

Having felt the impetus given by the work of Franklin and his associates to research in the field of non-aqueous solvents, the authors have planned a series of investigations upon the behavior of the hydronitrogens and their derivatives in liquid ammonia. Hydrazine, or hydrogen dinitride, as it might be called, obviously bears a relation to ammonia empirically similar to that borne by hydrogen peroxide to water,[3] while hydronitric acid, or hydrogen trinitride, may in a sense be regarded as analogous with the hypothetical higher oxides of hydrogen[4] concerning which there has been some recent discussion. In case the hydrogen pernitrides in liquid ammonia possess properties similar to those of hydrogen peroxide in aqueous solution it is to be expected that under proper conditions they should act in a sense as oxidizing agents, or more strictly as *nitridizing* agents. One ultimate purpose of the research has therefore been to study the phenomena of ammono-oxidation, or *nitridation*. Another purpose has been to investigate the phase rule relations, especially the pressure-concentration curves, in the two component systems (1) ammonia, hydrazine, (2) ammonia, hydronitric acid, (3) hydrazine, hydronitric acid, and in the three-component system ammonia, hydrazine, hydronitric

[1] *Z. physik. Chem.*, 29, 89–118 (1899); see also Goldschmidt, *Ann.*, 351, 108–33 (1907).

[2] This Journal, 27, 820–51 (1905), page 826.

[3] See Remsen, *Inorganic Chemistry*, 1899, 276. Brühl, *Ber.*, 30, 162–72 (1897). Angeli, *Atti accad. Lincei*, [5] 19, II, 29–36 or 94–101 (1910).

[4] Thénard, *Compt. rend.*, 75, 177 (1872). Berthelot, *Ibid.*, 90, 656–60 (1880). Bach, *Ber.*, 33, 1506–17, 3111–8 (1900); 34, 3851–5 (1901); 35, 158–60 (1902). Armstrong, *Proc. Chem. Soc.*, 16, 134 (1900). Baeyer and Villiger, *Ber.*, 33, 2488–97 (1900). Ramsay, *J. Chem. Soc.*, 79, 1324–6 (1901). Bach, *Ber.*, 35, 3424–5 (1902). Clover, *Am. Chem. J.*, 29, 463–74 (1903).

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acid. The first few articles of the series will be of an introductory character.

It seemed advizable at the outset to study the behavior of hydrazine sulfate, the compound of hydrazine most readily obtainable in a pure condition, in liquid ammonia. A vacuum beaker was provided with a tightly fitting cork, through which passed a large test tube, an inlet tube for liquid ammonia, and an outlet for ammonia gas. The test tube was closed with a cork provided with inlet and outlet tubes for ammonia, with a tube through which portions of the liquid could be siphoned off at will into sample tubes, and with platinized platinum electrodes for use in determining the conductivity of the solution obtained. The beaker, which served merely as a jacket for the test tube, was filled with crude liquid ammonia drawn directly from the steel container, and the test tube was partly filled with liquid ammonia obtained by condensing a current of the gas which had been dried over metallic sodium. A sample of recrystallized hydrazine sulfate (Raschig) weighing 0.73 gram was introduced into the test tube. The solid was soon observed to increase considerably in bulk, undergoing a sort of slaking process similar to that noted by Gore[1] and by Franklin[2] when the chlorides of magnesium, calcium, strontium, barium, zinc, cadmium, manganese, cobalt, nickel, and lead were treated with liquid ammonia. That considerable heat was evolved during this slaking process was evidenced by the rapid boiling, not only of the ammonia in the test tube, but also of that in the jacket.

The phenomena noted by Franklin in connection with the metallic chlorides were explained by him on the ground that in all probability the already known addition products of the respective salts with ammonia were obtained. In the case of calcium chloride this was demonstrated to be correct. It was at first supposed by the authors that this explanation would also hold true in the case of hydrazine sulfate. This idea seemed to be borne out by the fact that the specific conductivity of the ammonia as determined by the method of Kohlrausch[3] underwent but comparatively little increase during the progress of the experiment. After the reaction had gone to completion and the finely divided solid product had settled, several samples of from 3 to 5 cc. of the supernatant liquid were finally siphoned off into weighed test tubes, each of which was provided with a tightly fitting cork and a long glass tube with a crook at the end, to prevent diffusion of atmospheric air into the test tube during the evaporation of the liquid. After the liquid ammonia had completely evaporated,

[1] *Proc. Roy. Soc.*, 21, 140 (1873).
[2] *Am. Chem. J.*, 20, 820–36 (1898), page 822.
[3] *Wied. Ann.*, 64, 417 (1898). See also *Das Leitvermögen der Electrolyte*, page 1 (1898).

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and the test tubes had warmed up to room temperature, small volumes of a residual liquid were found in each case. In blank experiments, previously carried out under similar conditions with liquid ammonia to which no hydrazine sulfate had been added, no ponderable residues were obtained.

The liquid residues were found by analysis to consist chiefly of free hydrazine. Small amounts of sulfuric acid were also found, no doubt because of the carrying over of small amounts of the finely divided white solid during the process of siphoning the liquid. The solid residue in the large test tube in which the reaction had taken place continued to give off ammonia for some time after the liquid ammonia had disappeared. After the evolution of ammonia had ceased the shrunken mass of solid was by analysis shown to be ammonium sulfate containing a negligible amount of hydrazine. The solid as it appeared at first after the evaporation of the supernatant liquid was in all probability an ammonated ammonium sulfate, which underwent gradual deammonation as it warmed up to room temperature.

In order to subject the reaction to further investigation the apparatus shown in the accompanying sketch was constructed. The steel cylinder *A* served as the source of ammonia, which was led first through the tube *B*, about one meter long, filled with sodium wire. It then passed through *C*, which contained ignited asbestos, and through the stopcock *D* into the U-tube *E*, which was partly filled with glass beads. After the air had been displaced from the entire apparatus at the beginning of an experiment, the vacuum beaker *F*, filled with solid carbon dioxide and alcohol, was cautiously brought up around *E*, and sufficient ammonia to cover the beads with liquid was condensed. During the progress of the experiment the height of *F* was so adjusted as to keep the amount of liquid in *E* as nearly as possible constant.

After bubbling through the liquid ammonia in *E* the gas passed over into the condenser *G*, which was refrigerated by means of solid carbon dioxide and alcohol in the vacuum beaker *H*, where it was entirely liquefied. By suitable adjustment of the stopcock *D* it was found possible to deliver a steady drip or stream of liquid ammonia into the funnel tube *K*. Into this tube was placed, at the beginning of each experiment, a closely fitting extraction thimble containing a weighed amount of hydrazine sulfate. The delivery tube from the condenser passed through one of the three openings in a cork which was fitted into the top of a large reaction tube *L*. Through the other openings in the cork passed *P*, the outlet for gaseous ammonia, and *N*, the delivery tube for the liquid extract. Until ready for use the end of this tube was kept covered in order to prevent the introduction of air or of moisture into the apparatus. The reaction tube *L* was kept at the proper temperature by means of the vacuum beaker *M*, which was filled with solid carbon dioxide and alcohol.

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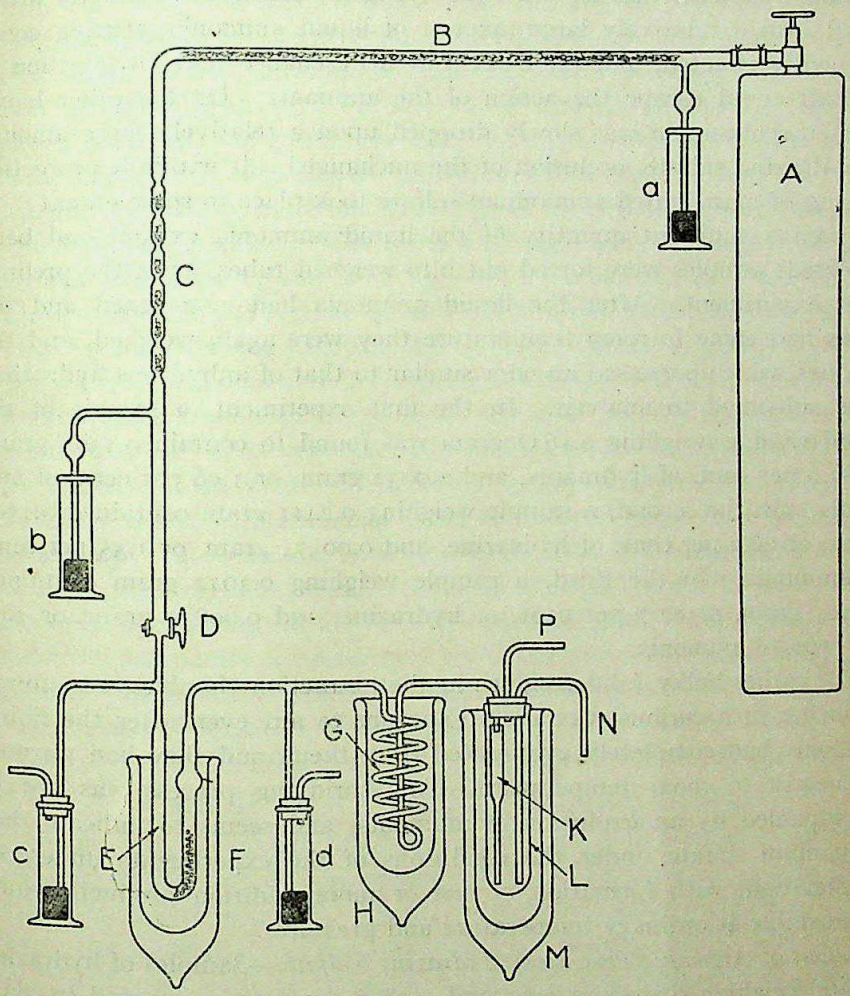
The mercury traps *a*, *b*, *c* and *d*, served as safety outlets. Various accessory devices have been omitted from the sketch for the sake of clearness.



Three experiments were performed in this apparatus, using weighed amounts of pure hydrazine sulfate. The sample was in each case introduced into the extraction thimble in the funnel tube *K*, and ammonia was allowed to drip upon it until the reaction, so far as could be seen, had proceeded to completion. By this time a considerable quantity of the liquid ammonia had accumulated in the lower part of *L*. No difficulty whatever was experienced in effecting a perfect separation of the finely divided white solid from the liquid. No sulfuric acid whatever was found in the extract. It was not found possible to effect so nearly quantitative a decomposition of the hydrazine sulfate in this apparatus as in the device in which the preliminary work was carried out, for the

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simple reason that in the preliminary work the "wet" method was employed and in the subsequent experiments the "dry" method. When the wet method was used, that is, when the hydrazine sulfate was directly introduced into a relatively large amount of liquid ammonia, stirring could be readily effected, and there was but little chance that any portion of the salt could escape the action of the ammonia. On the other hand, when the ammonia was slowly dropped upon a relatively large amount of hydrazine sulfate, occlusion of the unchanged salt within a protective coating of ammonated ammonium sulfate took place to some extent.

When a sufficient quantity of the liquid ammonia extract had been collected, samples were forced out into weighed tubes, as in the preliminary experiment. After the liquid ammonia had evaporated and the tubes had come to room temperature they were again weighed, and the residues, which possessed an odor similar to that of anhydrous hydrazine, were subjected to analysis. In the first experiment, a sample of the liquid residue weighing 0.1632 gram was found to contain 0.1364 gram, or 83.6 per cent. of hydrazine, and 0.0032 gram, or 1.96 per cent. of ammonia. In the second, a sample weighing 0.2411 gram contained 0.1599 gram, or 66.3 per cent. of hydrazine, and 0.00374 gram, or 1.55 per cent. of ammonia. In the third, a sample weighing 0.4042 gram contained 0.3341 gram, or 82.7 per cent. of hydrazine, and 0.00837 gram, or 2.07 per cent. of ammonia.

The rather bulky solid residues in the extraction thimbles were found to shrink in a curious way upon exposure to air, even after the liquid ammonia had completely evaporated from them, and they had warmed up nearly to room temperature. This shrinking process was always accompanied by an evolution of ammonia, and seems to indicate that ammonium sulfate under the conditions of the experiments undergoes ammonation, with formation of one or more addition products which are unstable at ordinary temperature and pressure.

Action of Ammonia Gas upon Hydrazine Sulfate.—Samples of hydrazine sulfate weighing 0.2616, 0.2427 and 0.1848 gram were exposed in glass stoppered U-tubes to a current of ammonia gas for several hours at a temperature of about 22°. After two hours the samples had gained respectively 0.0131, 0.0106 and 0.0116 gram; after five and one-half hours, 0.0291, 0.0187 and 0.0140 gram; after twelve hours, 0.0329, 0.0450 and 0.0170 gram. Small drops of a colorless, viscous liquid, probably a solution of hydrazine monosulfate in free hydrazine, appeared on the salt and on the walls of the tubes, but the reaction did not progress to an end, owing no doubt to the relative smallness of the active mass of ammonia. At higher pressures the equilibrium would undoubtedly be displaced in the direction of a higher concentration of free hydrazine.

Action of Liquid Ammonia upon Ammonium Sulfate.—In order to as-

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certain in a preliminary way whether ammonium sulfate unites with liquid ammonia under the conditions of these experiments, weighed samples of the salt were treated with liquid ammonia in glass stoppered U-tubes. These tubes were cooled with solid carbon dioxide to about —72°, and the liquid ammonia was permitted to stand in contact with the solid for some time. A slight swelling of the salt was noted, and a tendency for it to cake in the bottom of the tubes. Dry air was now caused to pass slowly through the tubes, which were still immersed beneath the refrigerant, until the escaping current was shown, with the aid of Nessler's solution, to be free from ammonia. The tubes were then closed, permitted to warm to room temperature, and were weighed. In the first tube the sample, which weighed 0.3375 gram at the outset, was found to have gained 0.0407 gram. In the second, the sample, which originally weighed 0.2853 gram, was found to have gained 0.0505 gram. The presence of an excess of ammonia in the samples was also directly shown by subsequent analysis. It is very probable therefore that the ammonium sulfate formed by the action of ammonia upon hydrazine sulfate forms an addition product with ammonia under the conditions of the experiments. No attempt will be made, however, to describe the composition of this product until certain pressure-concentration isotherms in the system ammonia, ammonium sulfate have been investigated. At ordinary temperatures and under a pressure of one atmosphere of ammonia gas the salt does not absorb appreciable amounts of the gas.

Discussion of Results.—The decomposition of hydrazine sulfate by the action of liquid ammonia may be explained with the aid of the equation

$$N_2H_4.H_2SO_4 + 2NH_3 \rightleftharpoons (NH_4)_2SO_4 + N_2H_4.$$

With ammonia as solvent, the active mass of that component is, of course, very large, and this in conjunction with the insolubility of ammonium sulfate in liquid ammonia[1] insures, under favorable mechanical conditions, the quantitative decomposition of the hydrazine salt. Lobry de Bruyn[2] has shown, on the other hand, that free hydrazine can displace ammonia from ammonium salts.

It is, of course, conceivable that the decomposition of hydrazine sulfate by the action of ammonia might involve a dissociation of the ammonia molecule, with initial formation of hydrazine amide, or some other compound of hydrazine with ammonia, and of sulfuric acid. Certain preliminary experiments performed in connection with the present research indicate that at —33° free hydrazine does hold a certain amount of ammonia rather tenaciously, but whether this is held in physical solution or in chemical combination cannot be stated until certain isotherms in the pressure-concentration diagram of the system ammonia, hydrazine

[1] Franklin and Kraus, *Am. Chem. J.*, 20, 820–36 (1898), page 823.

[2] *Rec. trav. chim.*, 15, 174–84 (1896), page 179.

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have been completely explored. This investigation is now in progress. Whether the decomposition of hydrazine sulfate by ammonia is to be regarded as a simple displacement of hydrazine by ammonia, or as a process involving dissociation of the ammonia molecule, it may, in the opinion of the authors, be looked upon as an instance of *ammonolysis*, *i. e.*, of the breaking up of a salt by the action of ammonia.

The reaction obviously suggests a new method for the preparation of free hydrazine from certain of its salts.

Summary.

In the present investigation it has been shown that hydrazine sulfate is decomposed by the action of liquid ammonia at —33° in accordance with the equation

$$N_2H_4.H_2SO_4 + 2NH_3 = (NH_4)_2SO_4 + N_2H_4.$$

The resulting solution of free hydrazine in liquid ammonia may be separated from the entirely insoluble ammonium sulfate (or its addition product with ammonia) by decantation or by filtration. This suggests a new method for the preparation of free hydrazine from certain of its salts. Even at ordinary temperatures, with relatively small active mass of ammonia, the reaction proceeds to an appreciable extent.

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BEHAVIOR OF THE HYDRONITROGENS AND THEIR DERIVATIVES IN LIQUID AMMONIA. II. AMMONOLYSIS OF CERTAIN HYDRAZINE SALTS.

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It has already been shown in this laboratory[1] that hydrazine disulfate when treated with liquid ammonia at —33° undergoes decomposition, yielding free hydrazine and ammonium sulfate. In conformity with the system of nomenclature used by Goldschmidt and Salcher[2] and by E. C. Franklin[3] this reaction, whether it involves the splitting of an ammonia molecule, with initial formation of hydrazine amide and sulfuric acid, or, as seems more probable, a simple displacement of hydrazine by ammonia in accordance with the law of mass action, has been considered to furnish a new instance of ammonolysis.

The present investigation has been undertaken with the purpose of ascertaining whether or not certain other hydrazine salts undergo ammonolysis in liquid ammonia. The compounds selected comprize a number of salts containing acids, the ammonium salts of which have previously

[1] THIS JOURNAL, 33, 1728 (1911).
[2] *Z. physik. Chem.*, 29, 89–118 (1899).
[3] THIS JOURNAL, 27, 820–51 (1905), page 826.

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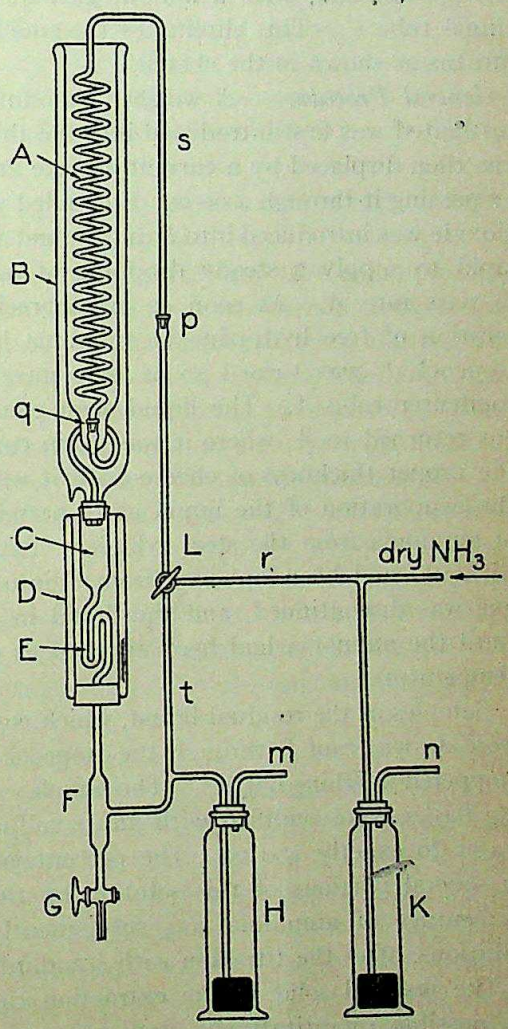
been shown to be insoluble in liquid ammonia.[1] The behavior of hydrazine monosulfate, hydrazine dioxalate, hydrazine diselenate, hydrazine monophosphate, and hydrazine diphosphate, respectively, in liquid ammonia has been investigated.

Apparatus Employed in the Experiments.—After considerable preliminary experimentation the form of apparatus shown in the subjoined sketch was adopted. This device, which virtually serves as a low temperature extraction apparatus, consists essentially of a spiral condenser tube, *A*, the upper end of which may be connected through the three-way stopcock *L* with a source of pure, dry ammonia, and which is surrounded by the vacuum cylinder *B*. The lower end of the spiral tube is connected through the ground glass joint *q* with an outlet tube which delivers into the cylindrical funnel tube *C*. This tube contains a closely fitted extraction thimble made of heavy filter paper, which is designed to hold the weighed sample of the hydrazine salt under investigation. The loop *E* serves to trap the liquid ammonia and to hold it for a time in contact with the hydrazine salt. The accumulation of liquid upon the salt greatly facilitates the process of ammonolysis and favors the removal of the free hydrazine formed.



After the ammonia has collected to a sufficient depth it is automatically siphoned from the thimble, and is delivered into the receiver *F*. The vacuum jacket *D* is used as a container for solid carbon dioxide, which serves to prevent evaporation of the liquid in *C* and *E*. The receiver is provided with a stopcock, *G*, through which samples of the product

[1] Franklin and Kraus, This Journal, 20, 820–36 (1898).

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may be removed, and with a side-arm, which communicates through *L* with the spiral condenser tube. The mercury traps *H* and *K* serve as safety outlets. For the sake of convenience in setting up or dismantling the apparatus the tube *s* is provided with the ground joint *p*. The spiral tube may, therefore, be removed by simply disconnecting at *p* and *q*. In its latest form the vacuum cylinder *B* has been provided, at its lower end, with a hollow, ground glass stopper that fits into the funnel tube *C*. This eliminates the small cork that was used in the apparatus as shown in the sketch.

General Procedure.—A weighed amount of the hydrazine salt to be investigated was first introduced into the thimble. All air in the apparatus was then displaced by a current of pure ammonia gas that had been dried by passing it through a 60 cm. tube filled with sodium wire. Solid carbon dioxide was introduced into *B* and *D*, and a current of ammonia, sufficiently rapid to supply a steady dropping of liquid upon the salt, was caused to pass into *A*. As soon as an appreciable quantity of the resulting solution of free hydrazine in ammonia had been delivered into *F*, the stopcock *L* was turned so as to connect the receiver with the spiral condenser tube *A*. The liquid soon commenced to evaporate, and the gas returned to *A*, where it was again condensed. By wrapping *F* with the proper thickness of cheese-cloth it was found possible so to regulate the evaporation of the liquid as to permit the cutting off of the supply of ammonia from the steel cylinder. After several successive quantities of liquid had been siphoned from *C* into *F* further condensation of the gas was discontinued, and the liquid in *F* was permitted to evaporate until the ammonia had been expelled as completely as possible at room temperature.

Samples of the residual liquid, which consisted chiefly of free hydrazine, were drawn from *F* through the stopcock *G*, and were weighed in glass stoppered weighing bottles. The samples were then transferred to measuring flasks, were acidified with dilute sulfuric acid, and were diluted with water to exactly 100 cc. The percentage of hydrazine was determined in several portions of this solution by the method of Rimini,[1] and the percentage of ammonia was subsequently determined in the residual solutions, after the titration with standard thiosulfate solution.

The residual solid in the extraction thimble was removed, as nearly as possible quantitatively, and was weighed. The entire sample was then dissolved in water and was diluted to a convenient volume. Hydrazine (if present), ammonia, and the acid of the salt used were determined in different portions of the solution.

Details of Individual Experiments.

Behavior of Hydrazine Monosulfate in Liquid Ammonia.—Since hy-

[1] THIS JOURNAL, 33, 1353–62 (1911).

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drazine disulfate has already been shown to undergo decomposition in liquid ammonia with formation of free hydrazine and ammonium sulfate, it has been considered likely that hydrazine monosulfate, a substance containing a much larger percentage of hydrazine than the disulfate, would undergo ammonolysis under similar conditions with even greater readiness.

The hydrazine monosulfate used in these experiments was prepared by neutralizing 15 grams of hydrazine hydrate (Raschig) with dilute sulfuric acid, using methyl orange as indicator. After the resulting solution had been evaporated on the water bath the monosulfate crystallized as a fine white powder. A small sample of the product was analyzed, with the following results:

N_2H_4, 39.4 per cent.; H_2SO_4, 60.8 per cent. Theory for N_2H_4 in $(N_2H_4)_2.H_2SO_4$, 39.5 per cent.; for H_2SO_4, 60.5 per cent.

A weighed sample of hydrazine monosulfate was placed in the extraction thimble, and a current of dry ammonia was swept through the apparatus in order to displace the air. During this operation the air was allowed to escape through the stopcock *G*. When the stopcock was finally closed, a surprizingly rapid diminution in pressure took place within the apparatus, in spite of the fact that a moderately rapid current of ammonia was still being admitted. This diminution in pressure occurred before any solid carbon dioxide was used, and resulted in the drawing of a considerable quantity of mercury from the trap *H* into the apparatus. On removal of the extraction thimble it was found that the hydrazine compound had become very moist and sticky as a result of the absorption of ammonia. When spread out and exposed to the air the moist substance gave off considerable quantities of ammonia, finally resuming its original appearance.

A second sample of the monosulfate weighing 6.8768 grams was placed in the thimble. The air in the apparatus was displaced as before, but the precaution was taken to introduce the ammonia with sufficient rapidity to prevent diminution in pressure as the ammonia was absorbed by the hydrazine compound. After the substance had been treated with liquid ammonia as described in a preceding paragraph, a sample of free hydrazine was obtained which, after the ammonia had evaporated as completely as possible at room temperature, was found by analysis to contain 93.2 per cent. of hydrazine. Tests were made for sulfuric acid, with negative results.

The residue in the extraction thimble continued to give off ammonia for some time after it had been removed from the apparatus. When this process had finally come to an end the residual substance was shown, by analysis of its three components, to contain 10.5 per cent. N_2H_4, 70.6 per cent. H_2SO_4, and 18.8 per cent. NH_3. From these facts it is apparent

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that hydrazine monosulfate very readily undergoes decomposition in liquid ammonia with formation of free hydrazine and ammonium sulfate. Under the conditions of this particular experiment, however, the process was not complete, since a portion of the hydrazine compound apparently escaped the action of the ammonia, probably owing to its enclosure within a protective coating of ammonated ammonium sulfate. The moist, sticky condition of the substance during the early stages of its ammonolysis was in all probability due to the liberation of hydrazine. The gradual drying of the mass on exposure to the atmosphere was presumably attributable to the displacement of ammonia from ammonium sulfate by the free hydrazine.[1]

Behavior of Hydrazine Monosulfate toward Ammonia Gas at Room Temperature.—From the peculiar behavior of the salt when first brought into an atmosphere of ammonia gas in the preceding experiment, it was considered probable that ammonolysis would take place to some extent even at ordinary temperatures. Preliminary experiments were first performed in which weighed samples of hydrazine monosulfate were treated in glass-stoppered U-tubes with dry ammonia gas for definit periods of time. It was found that the salt in every case absorbed very appreciable amounts of ammonia, becoming moist and sticky. Comparative tests with weighed samples of hydrazine disulfate showed that this substance also, under similar conditions, has a tendency to absorb ammonia, but rather more slowly than the monosulfate. A sample of hydrazine monosulfate that weighed 1.0189 grams increased in weight, after one hour's treatment, to 1.0819 grams. At the end of the second, third, and fourth hours, respectively, the sample weighed 1.0771, 1.0764 and 1.0767 grams. The loss in weight after the end of the first hour was undoubtedly due to the escape of hydrazine vapor with the current of ammonia. The presence of hydrazine in an absorbing solution located at the end of the chain of U-tubes was demonstrated at the conclusion of the experiment.

In order to separate the liquid formed by the action of dry ammonia upon hydrazine monosulfate, samples of the salt weighing respectively 3.9315 and 4.3704 grams were first treated with ammonia for an hour and a half, and were then centrifugalized for several minutes at an average rate of about one thousand revolutions per minute. This operation was carried on in special glass tubes made for the purpose, and mounted in a Bausch and Lomb centrifugal apparatus. In each case a clear, colorless, viscous liquid possessing the odor of anhydrous hydrazine was obtained which in the first experiment weighed 0.3474 and in the second 0.3573 gram. The results obtained on analysis of these products are as follows:

[1] Lobry de Bruyn, *Rec. trav. chim.*, 15, 174–84 (1896), page 179.

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(1) N_2H_4 48.4 per cent., NH_3 3.36 per cent., H_2SO_4 46.0 per cent.; (2) N_2H_4 51.3 per cent., NH_3 2.67 per cent., H_2SO_4 48.6 per cent.

From these data it would appear that the liquid in all probability consists essentially of a solution of hydrazine monosulfate in anhydrous hydrazine. The presence of the ammonia may perhaps be explained as a result of the solubility of the gas in the hydrazine. In order to test the first of these statements a number of qualitative experiments upon the behavior of hydrazine monosulfate and hydrazine disulfate toward anhydrous hydrazine were performed. Hydrazine monosulfate was found to be very soluble, and hydrazine disulfate was found to react immediately with the hydrazine, with liberation of considerable heat, and undoubtedly with formation of the monosulfate, which then went into solution. For example, when 5 grams of the disulfate were added to 2 cc. of anhydrous hydrazine, the temperature of the mass quickly rose to 95°, and very nearly all of the solid ultimately went into solution.

By repeated or continuous treatment of hydrazine monosulfate with ammonia gas it is very probable that yields of free hydrazine much larger than those recorded in the two preliminary experiments could be obtained. Further work on the ammonolysis of hydrazine salts by the action of ammonia at ordinary temperatures and at various pressures is projected, and will be made the subject of a future communication.

Behavior of Hydrazine Dioxalate in Liquid Ammonia.—The hydrazine dioxalate used in these experiments was prepared and analyzed in this laboratory by Dr. J. W. Turrentine.[1] A sample of this substance weighing 6.6634 grams was placed in the extraction thimble and was subjected to the action of liquid ammonia in accordance with the general procedure outlined in an earlier paragraph. After the ammonia had been expelled from the liquid extract as completely as possible at room temperature, the residual liquid was found by analysis to contain 86.8 per cent. N_2H_4, and 0.15 per cent. ammonia. It was not found possible to detect the presence of any oxalic acid in an aqueous solution of the extract.

The solid residue in the extraction thimble was tested for hydrazine by means of Fehling's solution, with negative results. The percentages of oxalic acid and ammonia were found by analysis to be 73.3 and 27.4 per cent. respectively (theory, $H_2C_2O_4$ in $(NH_4)_2C_2O_4$, 72.5 per cent.; NH_3, 27.5 per cent.).

From these results it is apparent that hydrazine dioxalate undergoes ammonolysis when treated with liquid ammonia, with formation of free hydrazine and ammonium oxalate.

Behavior of Hydrazine Diselenate in Liquid Ammonia.—The hydrazine diselenate was prepared by the method of Rimini and Malagnini.[2] A

[1] This Journal, 32, 579–88 (1910).
[2] *Gazz. chim. ital.*, 37, I, 261–6 (1907).

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sample of 93.6 per cent. hydrazine hydrate was diluted with water until a 50 per cent. solution of the hydrate was obtained, to which four volumes of alcohol were then added. Two volumes of alcohol were added to a sample of pure selenic acid weighing 10.31 grams. The two solutions were cooled to 0° and were then mixed. A white precipitate of hydrazine diselenate was formed, which was removed by filtration, was thoroughly washed with absolute alcohol and ether and was finally placed in a desiccator over metallic sodium. This product, however, almost immediately assumed a pink color which became very conspicuous after the material had stood overnight, owing to its partial decomposition with the formation of free selenium. A fresh sample was consequently prepared by the same method with the added precaution of cooling the two solutions with the aid of a freezing mixture.

A sample of the perfectly white product weighing 2.6094 grams was immediately transferred to the extraction thimble and was subjected to the action of liquid ammonia. The liquid extract was found to contain 66.5 per cent. of hydrazine and no appreciable amount of ammonia. The white solid residue in the extraction thimble was analyzed with results as follows: NH_3, 20.87 per cent.; H_2SeO_4, 80.9 per cent.; theory for NH_3 in $(NH_4)_2SeO_4$, 19.0 per cent.; for H_2SeO_4,[1] 81.0 per cent. These results show that hydrazine diselenate when treated with liquid ammonia is ammonolyzed with formation of free hydrazine and ammonium selenate.

Behavior of Hydrazine Monophosphate in Liquid Ammonia.—The hydrazine monophosphate was prepared according to the method of Sabanyeev[2] by neutralizing an aqueous solution of hydrazine hydrate containing 10 grams with a solution of phosphoric acid, using methyl orange as indicator. The resulting solution was evaporated over the water bath to a syrupy consistency, and was then cooled and stirred until crystallization took place. After the crystals had stood for a short time in the desiccator over metallic sodium, they were found by analysis to contain 25.2 per cent. N_2H_4 and 73.0 per cent. H_3PO_4. Theory for N_2H_4 in $N_2H_4.H_3PO_4$, 24.6 per cent.; for H_3PO_4, 75.4 per cent. After the substance had remained in the desiccator for four days analysis showed 25.3 per cent. N_2H_4 and 73.7 per cent. H_3PO_4.

A sample of hydrazine monophosphate weighing 9.1287 grams was subjected to the action of liquid ammonia in the usual way. No indication of the liberation of hydrazine was obtained. The receiver was thoroughly rinsed with water at the conclusion of the experiment but the liquid gave no test for hydrazine when treated with Fehling's solution.

[1] In determining the selenic acid, the method outlined in Olsen's "Quantitative Chemical Analysis," 1908, page 105, was employed.

[2] *Z. anorg. Chem.*, 17, 480–93 (1898), page 488.

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The contents of the extraction thimble were found to have undergone an appreciable increase in weight during the experiment. On analysis this residue was found to contain 23.15 per cent. N_2H_4, 67.2 per cent. H_3PO_4 and 7.23 per cent. NH_3.

Behavior of Hydrazine Diphosphate in Liquid Ammonia.—The hydrazine diphosphate was prepared by the method of Sabanyeev.[1] Fifty cc. of a solution of phosphoric acid containing 0.1494 gram per cc. were diluted with a solution of hydrazine hydrate, using methyl orange as indicator. After the end-point had been reached, 50 cc. more of the acid were added and the resulting solution was evaporated over the water bath. The syrupy liquid thus obtained was cooled by means of a freezing mixture and was stirred until crystallization took place. The crystallin substance was pulverized and was dried in a vacuum desiccator over metallic sodium. On analysis the following results were obtained: N_2H_4, 14.09 per cent.; H_3PO_4, 86.2 per cent. Theory for N_2H_4 in $N_2H_4.2H_3PO_4$, 14.05 per cent.; for H_3PO_4, 85.95 per cent.

A sample of hydrazine diphosphate weighing 7.9588 grams was treated with liquid ammonia as in the preceding experiments. The solution obtained by rinsing out the receiver with water at the close of the experiment gave no test for hydrazine. From this fact it is apparent that hydrazine diphosphate does not undergo ammonolysis under the conditions of the present experiment.

The solid residue in the extraction thimble was found to have undergone an appreciable increase in weight during the experiment. On analysis the substance was found to have the following composition: N_2H_4 13.96 per cent., H_3PO_4 84.7 per cent., NH_3 1.41 per cent.

In a duplicate experiment 13.3311 grams of hydrazine diphosphate were treated with liquid ammonia with results entirely similar to those just described.

The failure of hydrazine monophosphate and hydrazine diphosphate to decompose when treated with liquid ammonia with formation of ammonium phosphate and free hydrazine seems to point towards the supposition that these salts may be less soluble in liquid ammonia than is ammonium phosphate.

Summary.

In the present investigation it has been shown:

1. That hydrazine monosulfate, hydrazine dioxalate, and hydrazine diselenate, like hydrazine disulfate, decompose in liquid ammonia with formation of free hydrazine and the ammonium salt of the acid previously combined with the hydrazine.

2. That hydrazine monophosphate and hydrazine diphosphate do not decompose when treated with liquid ammonia.

[1] *Loc. cit.*, p. 489.

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3. That hydrazine monosulfate when treated with ammonia gas at room temperature undergoes ammonolysis to some extent, and that a liquid consisting essentially of a solution of hydrazine monosulfate in free hydrazine may be separated from the mixture by centrifugal action.

These facts may serve as the basis for a new method for the preparation of free hydrazine from its salts. Further work upon this phase of the investigation is projected.

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BEHAVIOR OF THE HYDRONITROGENS AND THEIR DERIVATIVES IN LIQUID AMMONIA. III. ACTION OF AMMONIUM TRINITRIDE UPON CERTAIN METALS.

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In his epoch-making work upon reactions in liquid ammonia, E. C. Franklin[1] makes the statement that "many acids, both oxygen acids and halogen acids, as a matter of course in the form of their ammonium salts, dissolve freely in ammonia to form solutions which exhibit certain truly acid properties, as follows: First, they discharge the color of an ammonia solution of phenolphthalein, which has been rendered alkaline by the addition of a small quantity of a base. Second, solutions of ammonium salts in ammonia dissolve sodium, potassium, calcium and magnesium with the evolution of hydrogen and the formation of the respective metallic salts in accordance with the general equation,

$$M + NH_4X = MX + NH_3 + H.$$

Third, many metallic oxides and certain basic salts, all members of both classes of compounds being insoluble in ammonia, dissolve in solutions of ammonium salts."

The present investigation has been undertaken with a view to ascertaining whether or not ammonium trinitride behaves in liquid ammonia solution toward metals in accordance with the generalization made by Franklin. In the prosecution of this work an incidental study of the following topics has been found necessary: (1) Methods of preparing pure ammonium trinitride, (2) method for conveniently carrying out at —33° the reaction between weighed amounts of a metal and of ammonium trinitride in liquid ammonia, and under such conditions that the gas evolved may be collected, measured, and analyzed without difficulty, and that the solid reaction product may be readily weighed and analyzed.

Preparation of Ammonium Trinitride.—Ammonium trinitride was first prepared by Curtius,[2] who saturated an alcoholic solution of diazohippuramide with gaseous ammonia, and precipitated the pure ammonium

[1] THIS JOURNAL, 27, 820–51 (1905), page 822.

[2] *Ber.*, 23, 3023–33 (1890), page 3033.

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trinitride from the alcoholic filtrate by the addition of ether.[1] Curtius also prepared the compound by the action of hot alcoholic ammonia upon certain acid azides.[2] Certain of the properties of ammonium trinitride have been studied by Curtius,[3] by Berthelot and Matignon,[4] by Hittorf,[5] by Bach,[6] and by Berthelot and Vieille.[7]

The method employed in this laboratory for the preparation of comparatively large amounts of ammonium trinitride involves three operations: (1) preparation of an anhydrous ethereal solution of hydronitric acid, (2) precipitation of ammonium trinitride from this solution by the action of a current of pure dry ammonia gas, and (3) evaporation of the ether from the filtered ammonium trinitride.

The first of these operations was carried out by extracting with ether in three successive portions, either (*a*) an aqueous solution of hydronitric acid prepared by distilling the acid from Raschig sodium trinitride which had been acidified with dilute sulfuric acid, or (*b*) an aqueous solution of sodium trinitride to which had just been added in the cold the theoretical quantity of dilute sulfuric acid. The ethereal solution was in either case dried by prolonged shaking with dehydrated copper sulfate, which was finally removed by filtration.

The second step was, in general, carried out in a large Erlenmeyer flask. Pure, dry ammonia gas was slowly bubbled through the ethereal solution until precipitation was complete, and finally the precipitated ammonium trinitride was filtered out and was stored in a vacuum desiccator which from time to time was alternately evacuated and filled with dry air, until the ether had completely evaporated. The product was analyzed as follows: a sample weighing 1.2445 grams was dissolved in water, and the solution was diluted to exactly 100 cc. Thirty cc. of this solution were found to contain 0.1045 gram of ammonia, which corresponds to 28.2 per cent. NH_3. The hydronitric acid in two 10 cc. samples was precipitated and weighed as silver trinitride,[8] yielding 0.3086 and 0.3084 gram of that substance. These results correspond to 71.43 and 71.48 per cent. Theory for NH_3 in NH_4N_3, 28.4 per cent.; for HN_3, 71.6 per cent.

Apparatus Employed in the Experiments.—The apparatus consisted essentially of the modified Schiff nitrometer *A*, provided with the three-way stopcock *K* through which communication may be established,

[1] *Ber.*, 24, 3341–9 (1891), page 3342.
[2] *Ibid.*, 29, 759–83 (1896), page 771.
[3] *Loc cit.*, and *J. prakt. Chem.*, [2] 58, 261–309 (1898), page 271.
[4] *Compt. rend.*, 113, 673 (1891).
[5] *Z. physik. Chem.*, 10, 593–620 (1892).
[6] *Ibid.*, 9, 241–263 (1892).
[7] *Ann. chim. phys.*, [7] 2, 339–351 (1894).
[8] THIS JOURNAL, 33, 1569–76 (1911).

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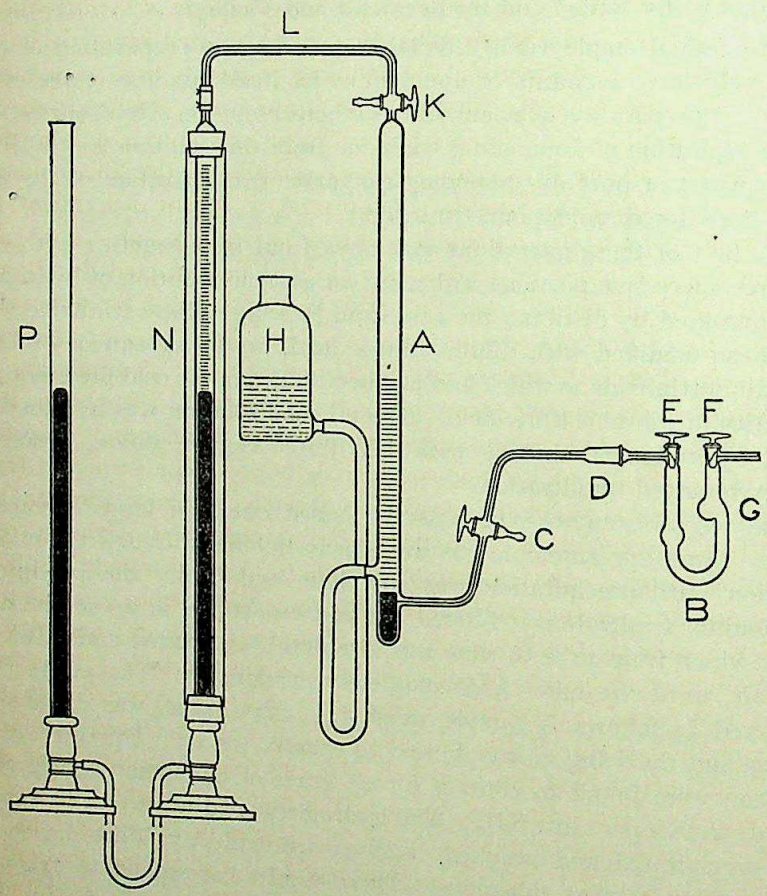
by means of the capillary tube *L* with the jacketed Hempel buret *NP*. The U-tube *B*, which was prepared from an ordinary glass stoppered U-tube by blowing a small bulb on one arm and the pocket *G* on the other, was connected with the nitrometer tube by means of the ground glass



joint *D*. Communication between *B* and *A* or between either of these tubes and the outer air could be established through the three-way stopcock *C*. The stopcocks *E* and *F*, which were originally hollow, were filled with paraffin in such a way as to prevent the trapping of gas during the aspiration of ammonia through the apparatus.

General Procedure.—The Hempel buret *NP* was first filled with the proper amount of clean, dry mercury, and the nitrometer tube *A* was provided with such an amount of mercury that there was no danger of drawing acid into *B* when the pressure in the U-tube was for any reason temporarily lowered. A 5 per cent. solution of sulfuric acid was introduced into *A* and into the level bottle *H*. The U-tube was thoroughly

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cleaned and dried and was weighed, first empty and then with a convenient sample of ammonium trinitride. By passing a current of pure, dry ammonia[1] through the U-tube all air was displaced and the stopcocks *E* and *F* were then closed.

A weighed sample of the metal under investigation was introduced into the pocket *G*, and the stopcock *F*, which had been removed for a moment, was replaced. During the handling of metals that were easily corroded by moist air, care was taken to protect the samples from exposure. By working very rapidly and by warming the weighing bottles, it was found possible to prepare weighed samples of the alkali metals sufficiently free from the oxide for the purpose of present experiments.

A current of pure, dry ammonia was now passed through the U-tube for some time, in order to displace the air that had entered during the introduction of the metallic sample. This current entered the apparatus through the side-arm of the stopcock *F* and left it at *C*. After the tube *A* had been filled with acid by raising *H* and suitably manipulating *K*, the stopcock *C* was so turned as to divert the current of ammonia into the nitrometer. In case the bubbles of gas were immediately absorbed by the acid solution, all air was considered to have been displaced from *B*. If, however, residual bubbles of appreciable size rose through the acid after the ammonia had been absorbed, the passage of the current was continued for a sufficient length of time to insure complete displacement of the air. A vacuum beaker containing solid carbon dioxide and alcohol was now cautiously raised about *B* until a sufficient quantity of ammonia had condensed to dissolve the ammonium trinitride. In certain cases it was found expedient to bring the metal into contact with the dry ammonium trinitride immediately after the air had been displaced and before the ammonia was liquefied. During these operations care was taken, either by regulating the speed of the flow of the ammonia gas or by varying the depth of immersion of the U-tube in the refrigerant, to keep the U-tube under a pressure as nearly as possible equal to that of the atmosphere. It is obvious that if condensation were so rapidly effected as to produce a partial vacuum in *B*, mercury, and ultimately acid, might easily be drawn over from the nitrometer.

The current of ammonia was finally interrupted by closing stopcock *F*, and the sample of metal was brought into contact with the solution of ammonium trinitride by gently tapping the U-tube. The gas evolved

[1] In connection with this operation a question concerning the possible formation of a compound of ammonia with ammonium trinitride naturally arizes. In an investigation completed some months ago the authors have found, by exploration of the pressure-concentration diagram, that ammonium trinitride forms a diammonate at —33°, which however decomposes at ordinary temperatures, and even at 0°. This compound, which has the formula $NH_4N_3.2NH_3$, or N_6H_{10}, and which is obviously a new hydronitrogen, will be described in the near future.

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during the reaction escaped through the stopcocks E and C into A. During the course of the reaction the temperature was so regulated as to permit slow evaporation of the solution. After the reaction had gone to completion, the evolved gas was completely transferred from B into A by means of a current of ammonia. The entire sample of gas was drawn from the nitrometer into the Hempel buret, and was then passed successively into pipets containing 5 per cent. sulfuric acid, and alkaline pyrogallol. The hydrogen in each sample was directly determined by passing the gas over palladium sponge. Throughout this analytical work care was taken to saturate with hydrogen all reagents that were brought into contact with the gas. The solution of sulfuric acid in the nitrometer tube was also saturated with hydrogen, and the gas was prevented from diffusing out of the liquid by passing a slow current of hydrogen through the level bottle so as to maintain an atmosphere of the gas above the liquid.

After the liquid ammonia in the U-tube had completely evaporated, and the gaseous ammonia had been completely expelled by means of a current of dry air, the U-tube was removed, externally dried, and was weighed. The solid contents of the tube were then removed and were subjected to analysis.

It was in general found convenient to perform simultaneous, double experiments in each case, using two entirely independent pieces of apparatus. In one of the U-tubes a slight measured excess of metal was in general present, and in the other an excess of ammonium trinitride.

It should, perhaps, be stated that it was not in any way the purpose of the present investigation to prepare and analyze the pure trinitrides of the various metals studied, since these substances have already been prepared by more convenient means. The object has been merely to ascertain whether or not the reactions take place in the sense of the general equation given by Franklin.

It will be noted that in several cases the volume of hydrogen obtained shows a deviation from theory that can by no means be explained by ordinary experimental error. This deviation is undoubtedly to be accounted for by the influence of two opposing factors. The first of these, which tends to lower the volume of hydrogen, depends upon the ability of nascent hydrogen to reduce hydronitric acid.[1] The second, which tends to increase the volume of hydrogen, depends upon the possible action of the excess of certain metals upon the ammonia itself, with formation of a metallic amide and free hydrogen.

If the metal under consideration is appreciably acted upon by dry

[1] Peratoner and Oddo, *Gazz. chim. ital.*, 25, II, 13 (1895); 30, II, 95 (1900). Szarvasy, *J. Chem. Soc.* (*London*), 77, 603 (1900). Cooke, *Proc. Chem. Soc.*, 19, 213 (1903). Dennis and Isham, THIS JOURNAL, 29, 18–31 (1907), page 28. Browne and Lundell, THIS JOURNAL, 31, 435–48 (1909).

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ammonia gas, it is quite possible that small amounts of hydrogen might be lost during the displacement of air by ammonia after the introduction of the metal into the U-tube.

It will also be noted that the weight of N_3 as determined in the residue is almost invariably appreciably smaller than the weight of N_3 in the ammonium trinitride used. This can by no means be explained as a result of experimental error, but is probably due in part to the reduction of hydronitric acid by nascent hydrogen, as noted in a preceding paragraph, and, in cases where an excess of the trinitride was used, in part to the volatilization of the ammonium trinitride[1] in the current of ammonia used to displace the air from the U-tube at the beginning, and in the current of dry air used to remove the free ammonia at the end of the experiment. This volatilization of ammonium trinitride may also help to explain in some cases the deficit in the volume of hydrogen evolved, as well as the repeated failure to detect ammonia in the residual solid even when an excess of ammonium trinitride was used at the outset.

Details of Individual Experiments. Action of Ammonium Trinitride upon Lithium.[2]—In each of the two experiments performed in connection with the present research an excess of metallic lithium was employed. In the first case 0.2077 gram of ammonium trinitride was caused to react with 0.0309 gram of lithium. The volume of hydrogen collected in the nitrometer tube, when reduced to standard conditions, amounted to 46.3 cc. Theory for hydrogen liberated from the ammonium trinitride used, 38.7 cc.; on the basis of the amount of lithium used, 49.9 cc. The residue in the U-tube weighed 0.1648 gram. After this had been dissolved in water and diluted to exactly 100 cc., two 20 cc. samples were analyzed for hydronitric acid, and were found to yield respectively 0.1025 and 0.1023 gram of AgN_3, corresponding to 87.1 per cent. N_3. The entire residue therefore contained 0.1435 gram N_3, while the ammonium trinitride taken at the outset contained 0.1453 gram N_3. No ammonia was found in the solid residue.

In the second experiment 0.3591 gram of ammonium trinitride was brought into contact with 0.0800 gram of lithium. The volume of hydrogen, reduced to standard conditions, was 52.0 cc. Theory for hydrogen on the basis of the ammonium trinitride used, 67.0 cc. Owing to an accident that resulted in the breaking of the U-tube at the conclusion of the

[1] Curtius and Rissom, *J. prakt. Chem.*, [2] 58, 261–309 (1898), page 272.

[2] The action of lithium upon ammonia itself has been studied by a number of investigators. See for example, Weyl, *Ann. Physik*, 121, 601 (1864). Seeley, *Chem. News*, 23, 169–170 (1871). Titherley, *J. Chem. Soc.* (*London*), 65, 504–22 (1894). Moissan, *Compt. rend.*, 127, 685–93 (1898); 128, 26 (1899); *Bull. soc. chim.*, [3] 21, 904 (1899); *Compt. rend.*, 133, 715 (1901). Lebeau, *Bull. soc. chim.*, [3] 27, 163 (1902). Ruff and Geisel, *Ber.*, 39, 828–43 (1906). Kraus, THIS JOURNAL, 30, 653–68 (1908). Ruff and Zedner, *Ber.*, 41, 1948–60 (1908).

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experiment, a satisfactory analysis of the solid residue could not be obtained. A sample was, however, tested for ammonia, with negative results. This indicates that the residue, aside from the excess of lithium, consisted of nothing but lithium trinitride.

The foregoing facts indicate that metallic lithium reacts with ammonium trinitride in liquid ammonia in the sense of the following equation:

$$Li + NH_4N_3 = LiN_3 + NH_3 + H.$$

Action of Ammonium Trinitride upon Sodium.[1]—In the first experiment 0.5034 gram of ammonium trinitride and 0.1725 gram of sodium were used. An excess of 0.0529 gram of the salt was therefore present. The characteristic blue color formed when the sodium was first brought into contact with the liquid ammonia solution very quickly disappeared, and a rather brisk evolution of gas took place. Under standard conditions the hydrogen occupied a volume of 79.7 cc. Theory for hydrogen, as calculated from the sodium used, 84.1 cc. This deficit in the amount of hydrogen is undoubtedly to be explained, in part at least, by the fact that in this particular experiment the nitrometer solution was not saturated with hydrogen and that the sample of gas was permitted to stand in the nitrometer for several hours before it was analyzed. In all other experiments error from this source was entirely eliminated. The solid residue, which weighed 0.5409 gram, was found to contain 0.3474 gram N_3. The ammonium trinitride used in the experiment contained 0.3522 gram N_3. No ammonia was present in the solid residue.

A sample of ammonium trinitride, weighing 0.1502 gram, was next brought into contact with an excess of sodium weighing 0.0942 gram. In this experiment, as was to have been expected, the color of the sodium solution persisted to the end of the experiment. The volume of hydrogen under standard conditions was 29.1 cc. Theory for hydrogen, on the basis of the ammonium trinitride taken, 28.0 cc.

An excess of ammonium trinitride weighing 0.2885 gram was caused to react with 0.0942 gram of sodium. The volume of hydrogen obtained,

[1] For information concerning the action of sodium upon ammonia reference should be made to the work of the following investigators: Wehl, *Pogg. Ann.*, 121, 601 (1864). Seeley, *Chem. News*, 22, 217 (1870); and 23, 169 (1870). Gore, *Proc. Roy. Soc.*, 20, 441 (1872). Joannis, *Compt. rend.*, 109, 900, 965 (1898); 110, 238 (1890); 112, 392–94 (1891); 113, 795 (1891); 114, 585–87 (1892); 115, 820–23 (1892); 116, 1370–73, 1518–21 (1893); 119, 557–59 (1894). Titherley, *J. Chem. Soc.* (*London*), 65, 504–22 (1894), page 504. Cady, *J. Physic. Chem.*, 1, 707–13 (1897). Hugot, *Compt. rend.*, 126, 1719–22 (1898); 127, 553 (1898); 129, 299, 388–90 (1899); *Ann. chim. phys.*, [7] 21, 5 (1900). Franklin and Kraus, *Am. Chem. J.*, 23, 277–313 (1900); 24, 83–93 (1900). Rengade, *Compt. rend.*, 138, 629–31 (1904). Chablay, *Compt. rend.*, 140, 1262–63, 1343–44, 1396–98 (1905). Lebeau, *Compt. rend.*, 140, 1042–44 (1905). Joannis, *Ann. chim. phys.*, [8] 7, 5–118 (1906). Ruff and Geisel, *Ber.*, 39, 828–43 (1906). Joannis, *Ann. chim. phys.*, 11, 101–10 (1907). Kraus, THIS JOURNAL, 29, 1557–71 (1907); 30, 653–68, 1197–1219, 1323–44 (1908). Ruff and Zedner, *Ber.*, 41, 1948–60 (1908).

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under standard conditions, was 44.4 cc. Theory as calculated from weight of sodium, 45.9 cc. The residue weighed 0.3157 gram and was found to contain 0.2007 gram N_3. Weight of N_3 taken, 0.2019 gram. Tests for ammonia in the residue yielded negative results.

From these facts it appears that metallic sodium reacts with ammonium trinitride in liquid ammonia in accordance with the equation:

$$Na + NH_4N_3 = NaN_3 + NH_3 + H.$$

Action of Ammonium Trinitride upon Potassium.[1]—The samples of ammonium trinitride and potassium used in the first experiment weighed respectively 0.3422 and 0.2351 gram. The potassium was therefore in excess. Volume of hydrogen under standard conditions, 64.5 cc.; theory, as calculated from the weight of ammonium trinitride, 63.8 cc. The residue weighed 0.4655 gram, and was found to contain 0.2220 gram N_3. Weight of N_3 taken, 0.2394 gram. The deficit in this case points toward a relatively large amount of reduction. It seems only fair to state, therefore, that the comparatively close agreement between the volume of hydrogen found and the theory for hydrogen is probably due to a balancing of the two sources of error mentioned in an earlier paragraph. The residue was tested for ammonia with negative results.

In another experiment an excess of ammonium trinitride weighing 0.2212 gram was caused to react with 0.1185 gram of potassium. Volume of hydrogen under standard conditions, 31.5 cc.; theory, as calculated from potassium used, 34.0 cc. The residue, which weighed 0.2528 gram, was found to contain 0.1466 gram N_3. Weight of N_3 taken, 0.1548 gram. No ammonia was found in the residue.

It is apparent from the foregoing results that metallic potassium reacts with ammonium trinitride in liquid ammonia as indicated by the equation:

$$K + NH_4N_3 = KN_3 + NH_3 + H.$$

Action of Ammonium Trinitride upon Calcium.[2]—In the first experiment 0.3150 gram of ammonium trinitride was brought into contact with an

[1] The behavior of potassium toward ammonia has been studied by the following investigators: Wehl, *Pogg. Ann.*, 121, 601 (1864); 123, 350 (1864). Seeley, *Chem. News*, 23, 169 (1870). Gore, *Proc. Roy. Soc.*, 20, 441 (1872). Joannis, *Compt. rend.*, 109, 900, 965 (1889); 110, 238 (1890); 113, 795–98 (1891); 114, 585–87 (1892); 115, 820–23 (1892); 116, 1370–73, 1518–21 (1893); 118, 713–16 (1894); 119, 557–59 (1894). Titherley, *J. Chem. Soc.* (*London*), 65, 504–22 (1894), page 511. Hugot, *Compt. rend.*, 129, 299–302 (1899); 129, 388–90, 603–5 (1899); *Ann. chim. phys.*, [7] 21, 5 (1900). Franklin and Kraus, *Am. Chem. J.*, 23, 277–313 (1900); 24, 83–93 (1900). Rengade, *Compt. rend.*, 138, 529–31 (1904). Joannis, *Compt. rend.*, 140, 1243–1245 (1905). Chablay, *Compt. rend.*, 140, 1396–98 (1905). Joannis, *Ann.*, [8] 7, 5–118 (1906). Ruff and Geisel, *Ber.*, 39, 828–43 (1906). Joannis, *Ann. chim. phys.*, 11, 101–10 (1907). Kraus, THIS JOURNAL, 29, 1557–71 (1907); 30, 653–68, 1323–44 (1908). Ruff and Zedner, *Ber.*, 41, 1948–60 (1908).

[2] In connection with the action of calcium upon ammonia the following articles

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excess of metallic calcium weighing 0.1249 gram. Volume of hydrogen under standard conditions, 55.7 cc. Theory, on the basis of the ammonium trinitride used, 58.8 cc. The residue, which weighed 0.3684 gram, was found to contain 0.2162 gram N_3. Weight of N_3 used, 0.2204 gram. Although a current of dry air had been passed through the U-tube for half an hour after the liquid ammonia had completely evaporated and the tube had warmed up to room temperature, the residue was still found to give off ammonia. Analysis showed that the total residue contained 0.0540 gram, or 14.7 per cent. of ammonia.

In a second experiment a slight excess of ammonium trinitride weighing 0.2071 gram was treated with a sample of calcium weighing 0.0690 gram. The total volume of gas obtained measured, after the absorption of ammonia with dilute sulfuric acid, and reduction to standard conditions, 38.0 cc. The residue weighed 0.2416 grams and was found to contain 0.1438 gram N_3. Weight of N_3 in ammonium trinitride taken, 0.1449. In this experiment a current of dry air was passed through the U-tube after the reaction had taken place, for seventy-five minutes, at the end of which period no ammonia could be detected with the aid of Nessler's solution in the air as it escaped from the tube. The residue was nevertheless found to contain 0.0266 gram, or 11.0 per cent. of ammonia.

From these results the conclusion may be drawn that metallic calcium reacts with ammonium trinitride in liquid ammonia in the sense of the equation

$$Ca + 2NH_4N_3 = Ca(N_3)_2 + 2NH_3 + 2H.$$

The calcium trinitride apparently unites with ammonia to form an ammonate, which, however, undergoes gradual deammonation in a current of dry air at ordinary temperatures.

Action of Ammonium Trinitride upon Magnesium.[1]—In the experiments with magnesium some difficulty was experienced in causing the reaction to proceed to completion. Because of the lightness of the metal, and because of its comparative insolubility in liquid ammonia, the sample was frequently carried upward by the brisk evolution of gas so as to adhere to the walls of the tube above the solution.

In the first experiment, 0.3986 gram of ammonium trinitride was treated with a sample of magnesium weighing 0.0471 gram. The volume of

should be consulted: Moissan, *Compt. rend.*, 127, 685–93 (1898); *Bull. soc. chim.*, [3] 19, 947 (1898); *Ann. chim. phys.*, [7] 18, 289–351 (1899); *Bull. soc. chim.*, [3] 21, 904–11 (1899); *Compt. rend.*, 133, 715–17 (1901); *Bull. soc. chim.*, [3] 27, 423–25 (1902). Lebeau, *Compt. rend.*, 140, 1042–44 (1905). Kraus, THIS JOURNAL, 30, 653–68 (1908).

[1] For the behavior of magnesium toward ammonia, the following references may be consulted: Briegleb and Geuther, *Ann.*, 123, 228–41 (1862). Warren, *Chem. News*, 58, 297–98 (1888). Merz, *Ber.*, 24, 3940–44 (1891). Kraus, THIS JOURNAL, 29, 1557–71 (1907).

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hydrogen under standard conditions was 45.6 cc. Theory, as calculated from weight of magnesium used, 43.4 cc. The residue was found to contain a large amount of ammonia.

In order to ascertain whether the magnesium trinitride formed undergoes ammonation under the conditions of these experiments, the residues obtained in two additional experiments were analyzed as follows: in the first case a residue weighing 0.2972 gram was found to contain 0.1513 gram or 50.9 per cent. N_3. Weight of N_3 in ammonium trinitride taken, 0.1512 gram. The percentage of magnesium was 9.68 and the percentage of ammonia, 38.76. In the second case, 0.2692 gram of residue was found to contain 0.1424 gram or 52.9 per cent. N_3. Weight of N_3 in ammonium trinitride used, 0.1434 gram. In this experiment 9.9 per cent. of magnesium and 34.9 per cent. of ammonia were found.

These facts indicate that while magnesium reacts with ammonium trinitride in liquid ammonia in the manner expressed by the equation

$$Mg + 2NH_4N_3 = Mg(N_3)_2 + 2NH_3 + 2H$$

the magnesium trinitride formed probably unites with ammonia to form an ammonate.

Behavior of Ammonium Trinitride toward Zinc, Aluminium and Tin.

Zinc.—A sample of ammonium trinitride weighing 0.4605 gram was brought into contact with a sample of zinc weighing 0.2497 gram. During the progress of the treatment, which lasted for three hours, no evidence could be obtained that a reaction had taken place. No appreciable amount of gas was evolved, nor was the U-tube found to have undergone any significant change in weight after the liquid ammonia had been evaporated. After the removal of the sample of zinc, tests for that element were made upon the residual contents of the tube, with entirely negative results. A duplicate experiment was performed with the same results.

Two further experiments were now conducted under conditions similar to those of the foregoing except that a small piece of platinum foil was introduced into the U-tube in each case so as to be in contact with the sample of zinc. Small bubbles soon began to form upon the surfaces of the zinc, but the reaction proceeded so slowly that at the end of two and one-half hours only about 2 cc. of gas were collected in each case. The presence of zinc in the residues was established after the samples of the metal had been removed from the U-tubes.

Aluminium.—No action whatever was observed when weighed samples of aluminium were brought into contact with weighed amounts of ammonium trinitride dissolved in liquid ammonia. Even when active aluminium was used purely negative results were obtained. In order to be certain that the metal was really active the samples were removed

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from the U-tubes at the conclusion of the experiments and were immersed in water. In each case immediate evolution of hydrogen was observed.

Tin.—A weighed sample of tin was kept in contact with a solution of ammonium trinitride in liquid ammonia for four hours. No action was observed to take place, and the presence of tin in the residual solid after the metallic sample had been removed could not be detected.

Summary.

In the present investigation it has been shown that:

1. Metallic lithium, sodium, potassium, calcium, and magnesium react vigorously with a liquid ammonia solution of ammonium trinitride, with formation of the respective trinitrides and with liberation of ammonia and hydrogen in accordance with the general equation given by Franklin.

2. Zinc does not react perceptibly with ammonium trinitride in liquid ammonia. In contact with platinum, however, a very slow reaction takes place.

3. Aluminium (both ordinary and active) and tin undergo no perceptible reaction when brought into contact with a solution of ammonium trinitride in liquid ammonia.

In order to facilitate the gasometric study of such reactions as the foregoing, a modified Schiff nitrometer has been designed, in which (*a*) weighed amounts of two solids may be brought together in liquid ammonia in the absence of air and moisture, (*b*) the evolved gases may be collected, measured, and preserved for subsequent analysis, and (*c*) the residual solid may be weighed and preserved or prepared for analysis.

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POTASSIUM: ITS TITRIMETRIC ESTIMATION IN SMALL AMOUNTS.

BY LEON T. BOWSER.

Received August 29, 1911.

There are in present use two colorimetric methods for the estimation of small quantities of potassium. One depends upon the red color developed by a potassium iodide solution to which potassium chloroplatinate is added, the other upon the yellow color developed by stannous chloride under the same conditions. Both are unduly sensitive to exterior conditions and even with the greatest of care it is very often impossible to obtain satisfactory results. The writer knew of a case where a set of determinations was spoiled by fumes from a fresh coat of paint in the room. While in some few laboratories no difficulties are encountered, in numerous others neither of these methods can be used; hence there is need of one indifferent to any but the most unusual of exterior conditions.

After the development of the qualitative method described in the pre-

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vious paper[1] an effort was made to apply it to quantitative work. The reaction does not lend itself either to colorimetric or turbidity methods on account of the very dark color of the reagent, and several other plans also failed. A method was finally worked out, involving precipitation of potassium as dipotassium sodium cobaltinitrite, filtering under appropriate conditions, and titrating the precipitate by means of very dilute potassium permanganate. After working out the proper conditions this procedure proved very satisfactory.

Among other things the cobaltinitrite method, as applied to larger amounts, calls for evaporation of the potash solution with excess of the reagent, but for several reasons this is not advizable with small amounts of potassium. Evidently there was needed a way of throwing down the yellow triple nitrite without evaporation, and of accurately measuring its amount after precipitation. Before finding just the requisit conditions numerous tests were made and many interesting facts were learned. Thus it was found that if to a potassium solution there be added strong acetic acid, then reagent, no precipitate appears, but when the reagent is added first, followed by acetic acid, a very good precipitate is obtained.

It was also found that certain reagents, notably alcohol and glacial acetic acid, act as accelerating agents, rendering the precipitation rapid and more or less complete. Alcohol alone gives complete precipitation when added to a mixture of potash solution and sodium cobaltinitrite reagent, but the precipitate is in such a finely divided condition as to render filtration extremely difficult and washing nearly impossible on account of the tendency to run through the filter. Titration results are high and evidently the conditions of precipitation abnormal, since consistent results are not obtainable. With acetic acid, on the other hand, the precipitate is of a coarse, granular nature and gives not the slightest hint of difficulty in washing. Unfortunately, however, precipitation is incomplete and far from uniform, while at the same time there is fairly rapid decomposition of both precipitate and reagent upon standing for a short period. There seems to be no other reagent answering the requirements as satisfactorily as either of these.

A study of the peculiarities of behavior of each of these reagents shows that they are supplementary, so to speak, alcohol giving complete precipitation and acetic acid incomplete, alcohol a poor texture of precipitate and acetic acid a very good one. This indicated that a mixture of the two might combine their good qualities, and trials showed such to be the case. The best results are attained when the mixture contains equal parts of glacial acetic acid and 95 per cent. alcohol, designated for the sake of convenience as acid-alcohol.

[1] THIS JOURNAL, 33, 1566 (1911).

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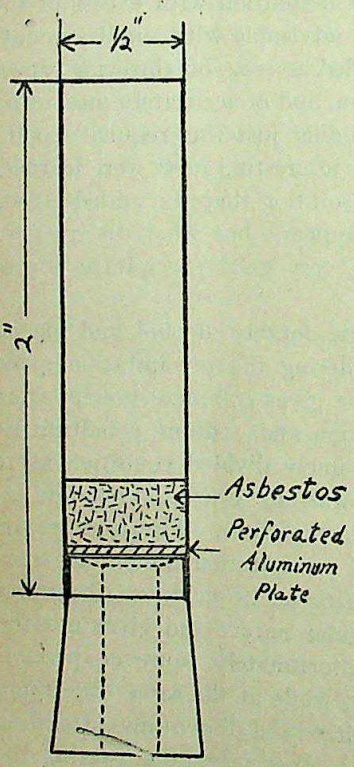
The minimum quantity of precipitating reagent allowable was found to be about 2.5 cc.; larger volumes do no harm but smaller ones give incomplete precipitation. The precipitating reagent dipotassium sodium cobaltinitrite, is prepared as described in numerous other papers,[1] and the details are unnecessary here.

The technic of the method finally adopted is as follows: The solution in which potassium is to be determined is evaporated nearly to dryness in a beaker, cooled, and to it added 2.5 cc. of sodium cobaltinitrite solution and 10 cc. of acid-alcohol, followed by agitation of the beaker. The precipitate is filtered under suction, not allowing it to remain for more than half an hour in contact with the reagent. The filter used is of the Shimer form, the dimensions being given in the figure. The excess of reagent is washed out by means of 20 per cent. acetic acid.



The asbestos pad bearing the precipitate is now pushed out into the beaker in which the precipitation was made, the filter tube rinsed with a few cc. of water, and the aluminum filter plate taken out and rinsed. An excess of 0.005 *N* potassium permanganate is run in, the solution is brought to boiling accompanied by stirring and the nitrous acid of the precipitate released by means of 1 cc. of sulfuric acid (1 part conc. acid : 1 part water). Heating and stirring are continued for a moment, then the excess of permanganate is titrated back by means of 0.005 *N* oxalic acid, if necessary adding more permanganate to get the end-point. After deducting a blank for asbestos, sulfuric acid, etc., the number of cubic centimeters of permanganate used, multiplied by 0.00004282, gives grams of K_2O, or by 0.00003554 gives grams of K.

A considerable portion of the procedure for potassium was subsequently adapted to the estimation of calcium, and the details of the latter method have already been published.[2] In that paper is given a full description of the burets used and of the titration blank on asbestos, but to avoid

[1] Adie and Wood, *J. Chem. Soc.*, 77, 1076. Sutton, "Volumetric Analysis," ninth edition, pp. 61–3. Bowser, *J. Ind. Eng. Chem.*, 1, 791.
[2] *J. Ind. Eng. Chem.*, 3, 82 (1911).

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the necessity of referring back, such of the description as pertinent will be quoted.

"All titrations are carried out with the titrated solution kept at nearly the boiling point. With a little practice the end-point of this reaction may be noted easily and with precision. From the results of the titration, a blank, to be determined by a separate titration, must be deducted as an allowance for permanganate consumed by the asbestos, water and sulfuric acid used. The first blank titration of a pad of asbestos oxidizes out practically all the impurities," and subsequent titrations establish the real blank to be deducted. "Practically all of the permanganate consumed is due to the 1 cc. of sulfuric acid used, as ascertained by a number of trials, hence there is necessity for care that exactly the same amount be used every time."

In the case of the calcium method practically the same amount of permanganate is used up in successive blanks, and the tenth titration will give about the same as the second. It is not so with the potassium method; there are considerable differences between successive titrations and these differences follow no rule whatever, hardly ever being twice the same. For this reason it is necessary to carry out a blank titration on the asbestos before each filtration. In actual analytical practice the asbestos from a preceding determination is poured into the filter tube made into a pad, and well washed with distilled water or 20 per cent. acetic acid. It is then rinsed into a beaker and titrated as in a determination, after which it is again made into a pad and used for filtering the potassium precipitate, the results of the blank titration being afterward subtracted from those obtained in the titration of the precipitate. This procedure, if judged from the written description, might appear to be bothersome and time-consuming, but it is in reality very simple and quickly carried out, as a few trials will prove.

The burets used in this titration are more strictly cataloged as graduated pipet. "For the most accurate work a small one graduated in fiftieths or hundredths is to be preferred, and this may, if desired, be read to two-hundredths of a cc. There is in use here a 2 cc. size graduated in fiftieths for permanganate, and a 1 cc. graduated in hundredths for oxalic acid. Both are fitted with tips drawn out so fine that the drops are very small, a size such that ten drops of solution equal 0.15 cc. is very satisfactory. A short rubber tube between the buret and small tip, with a glass bead in the tube to take the place of the more usual stopcock, gives a very delicate and satisfactory control of the rate of flow. The buret is filled by inserting the tip in the desired solution and drawing it up by suction, taking care to avoid contamination in any way."

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In Table I are shown the results from a number of titrations on potassium salts alone. Figures are parts per million of potassium.

TABLE I.

Calculated.	Found.	Calculated.	Found.	Calculated.	Found.	
25.00	26.13	7.12	6.62	1.000	0.854	a
	24.92		6.80		0.710	a
	26.25		7.21		1.150	a
	26.32		6.76		0.783	a
	25.37		6.71		0.815	b
	24.56		7.63		0.822	b
	24.52		6.99		0.815	b
	25.48		7.69		0.861	b
Av.....	25.44		7.05		0.874 (a) 0.828 (b)	

(a) using 10 cc. K solution
(b) using 50 cc. K solution

On the whole these results are quite satisfactory considering the small amounts involved.

To test the method in the presence of other metals, determinations were made in which potassium, sodium, calcium and magnesium were present in equal amounts. The results are shown in Table II, figures being parts per million as before.

TABLE II.

Calculated.	Found.	Calculated.	Found.	Calculated.	Found.
50.00	50.57	20.00	20.57	3.50	3.70
	51.20		20.04		3.27
	51.66		20.48		3.27
	48.05		...		..
Av.....	50.37		20.36		3.45

The presence of these metals has no appreciable effect on the amount of potassium found by titration, at least not when in moderate amounts.

Attempts were made to compare this method with the colorimetric one using potassium iodide, but unfavorable exterior conditions made it impossible to secure results by the latter. By the titration method very consistent results were obtained, the unfavorable conditions seemingly failing to affect it. So far as found the only difficulty encountered is when heavy ammoniacal fumes are in the air, and as a matter of ordinary precaution no estimations should be undertaken under such conditions.

Very satisfactory duplicates are obtainable by this method, and it is hoped that it may be found much better adapted to ordinary laboratory conditions than the colorimetric methods. It is very simple, the manipulations are few and easy, and the results are dependable. In concluding,

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it may well be noted that up to the present all attempts to apply this or any similar procedure to the estimation of larger amounts of potassium have proved futil.

DAYTON, O.

THE INFLUENCE OF THE MAGNETIC FIELD ON PASSIVE NICKEL AND IRON.

BY HORACE G. BYERS AND AGNES FAY MORGAN.

Received August 10, 1911.

In a previous article[1] it was shown that when using iron as an anode in various electrolytes the density of the current required to produce the passive condition is very materially increased when the anode is placed in a magnetic field. The amount of current required varied not only with the intensity of the field but also with different electrolytes and with the length of time of exposure of the iron to the electrolyte and perhaps with other factors; but in every case the required current density per square centimeter was greater in the magnetic field than out of it. A natural development of this work was an investigation of similar nature with nickel and steel as anodes.

In view of the rather rare instances of magnetic effects upon chemical action a brief summary of the literature of the subject may be in place. So far as we are aware the first contribution was by Professor Remsen[2] who showed that iron in a solution of copper sulfate is protected at the ends when in a magnetic field. Rowland and Bell[3] explain the action on the supposition that more energy is required to remove the iron from points nearest the magnetic poles induced by the magnetic field. They also present experimental evidence in support of their conclusion. Wolff[4] explains the protection on the basis of an accumulation of iron salts at the magnetic poles.

The articles cited all deal with a *protection* of iron from chemical action by magnetization. On the other hand Nichols and Franklin in a series of articles[5] call attention to the destruction of the passive condition of iron, when in concentrated nitric acid, by means of a magnetic field and take issue with the explanations offered by Rowland and Bell.[6] Andrews[7] showed that magnetized steel and unmagnetized steel show differences of potential in nitric acid (sp. gr. 1.42) of approximately 0.03 volt, at low temperatures the magnet being positive, while at 90° the voltage

[1] Byers and Darrin, THIS JOURNAL, 32, 750 (1910).
[2] *Am. Chem. J.*, 3, 157 and 6 (1881 and 1885).
[3] *Am. J. Sci.*, [3] 36, 39 (1888).
[4] *Am. Chem. J.*, 17, 122 (1895).
[5] *Am. J. Sci.*, [3] 31, 272 (1886); [3] 34, 419 (1887); [3] 35, 290 (1888).
[6] *Loc. cit.*
[7] *Proc. Roy. Soc. London*, 48, 116 (1891).

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rizes to 0.3 volt and the direction of the current is reversed. He also showed[1] that magnetized steel dissolves more rapidly in copper chloride solutions than unmagnetized bars of the same steel. Brendt[2] investigated the heat of solution of iron within and without the magnetic field and discovered no measurable differences. Duhem[3] deduces the theoretical conclusion that the heat of solution should be very slightly smaller in the field.

Experimental.

Nickel.—The nickel used in the following experiments was Merck's "100 per cent. thin wire" and a plate of "Rein nickel" rolled into a thin sheet. The apparatus used is as shown in the cut. The magnet was

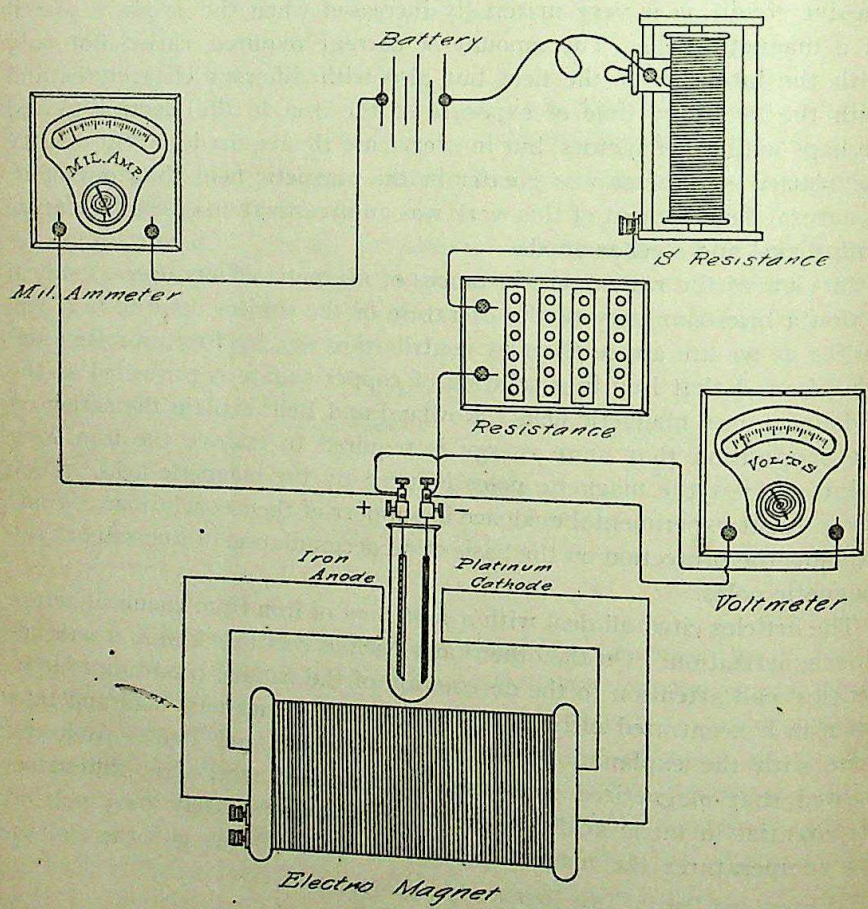

FIG. 1.

[1] *Proc. Roy. Soc. London*, 52, 114 (1893).
[2] *Z. physik. Chem.*, 9, 512 (1906).
[3] *Ziel und Struktur der physikalischen Theorien.*

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the same as that used by Byers and Darrin.[1] The electrodes were made by sealing the wires into glass tubes by means of paraffin. The current source was three U. S. storage cells. The current passing was read by means of Weston milliammeter with a scale of 150 and graduated to $^1/_2$ milliamperes. A key, not shown in cut, was used in circuit with the voltmeter and was only used to define the transition point from active to passive condition.

Several undetermined factors combine to render the results less accurate than could be desired, *viz.*, the rise of temperature due to the heating of the magnet when in action, the variation in the method of changing resistance, which seems to cause variation in transition points, the variation in the size of the electrodes by gradual solution while active and in the use of plates of different quality from the wire. The effect of stirring the electrolytes was also undetermined. The work shows that these, and perhaps other variables prevent exact duplication of results but the uniform character of the effect observed is unmistakable and represents, at least qualitatively, the effect of the magnetic field on the current density required to render nickel passive. The operation was as follows: the platinum nickel couple was inserted in a test tube containing the electrolyte and connected with the storage cells and ammeter, using a resistance sufficiently great so that the amount of current passing is less than sufficient to render the nickel passive. Without undue delay the resistance in the circuit was then diminished by means of the resistance box until the passivifying density was nearly reached, the final adjustment being made by the slide-wire resistance. When, after several trials, the exact current density required to produce passivity of the nickel anode was determined (a result indicated by a sudden drop of the reading on the ammeter, a rise in the voltmeter reading and the appearance of bubbles on the nickel) the anode was measured and the result recorded. The nickel was then rendered active by breaking the circuit and removal of the anode. (NOTE.—If a sufficient time is not allowed for the nickel to become thoroughly active, the density of the current required to again produce the passive state is greatly lessened. It will be observed that this fact increases the certainty of the results detailed.)

The couple is then replaced in the electrolyte and the experiment repeated exactly as before with the exception that the test tube is placed between the poles of the magnet and the new density of current determined and the area of anode remeasured. It should be mentioned that any diminution of area would tend to diminish the apparent density required, which fact renders the increased current more striking.

The results obtained will be given in detail for nitric acid and the results summarized thereafter, only the summaries being given.

[1] *Loc. cit.*

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A. Results with nitric acid.

TABLE I.

Electrolyte 10 per cent. HNO_3. Anode nickel wire 1 cm. exposed.

Without magnetic field.				In magnetic field.			
Diameter of anode.	Current required to cause passivity in milliamp.	Surface.	Current per sq. cm.	Diameter.	Current for passivity in milliamp.	Surface.	Current per sq. cm.
0.049	122	0.154	792	0.048	141	0 151	933
0.046	125	0.1445	868	0.045	148	0.140	1057
0.042	126	0.134	940	0.0445	125	0.139	900
0.040	104	0.1256	832	0.043	143	0.135	1051
0.038	115	0.119	966	0.0425	128	0.1346	955
0.0355	103	0.115	927	0.040	121	0.1256	968
0.033	95	0.1036	922	0.035	136	0.110	1236
..	...	..	...	0.033	111	0.1036	1077
..	...	..	...	0.031	115	0.097	1185

SUMMARY.

Without magnetic field.		In magnetic field.		
Number of experiments.	Average current per sq. cm. in milliamp.	Number of experiments	Average of rent per sq. cm. in milliamp.	Increase due to field.
7	892	9	1051	159

TABLE II.

		Without magnetic field.		In magnetic field.		
Electrolyte:	Anode.	No. of experiments.	Current per sq. cm. in milliamp.	No. of experiments.	Current per sq. cm.	Increase due to field.
5 per cent. HNO_3	Nickel wire	4	465	3	726	261
1 per cent. HNO_3	Nickel wire	5	247	2	324	77
5 per cent. HNO_3	Nickel plate	2	297	2	385	88

TABLE III.

		Without magnetic field.		In magnetic field.		
Electrolyte.	Anode.	No. of experiments.	Current per sq. cm.	No. of experiments.	Current per sq. cm.	Increase due to field.
5 per cent. H_2SO_4.....	Nickel wire	7	450	5	550	100
10 per cent. H_2SO_4.....	Nickel wire	8	471	6	627	156
10 per cent. H_3PO_4.....	Nickel plate	1	46	1	51	5
5 per cent. H_3PO_4.....	Nickel plate	2	39.7	2	42.1	2.4
N $NaNO_3$.....	Nickel plate	2	3.71	2	4.46	0.75
0.1 N $NaNO_3$.....	Nickel plate	2	2.81	2	3.13	0.32
0.5 N K_2SO_4.....	Nickel plate	8	2.38	10	3.00	0.62

Steel.—In the following experiments the anodes used were of steel and were made from large knitting needles, broken into convenient lengths, or of watch-springs straightened and cut into suitable pieces. The amount of carbon was not determined with exactness, but the needles were of much the softer steel. The anodes were covered as before with paraffin

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with the exception of a measured portion at one end. The current density required to render a piece of steel passive was first determined and then the anode was placed across the poles of the electromagnet and after about five minutes was removed and the passive point again determined. The polarity of the end used was determined by means of a compass needle. The individual results varied somewhat, as was to be expected, but on the whole were remarkably uniform and always of the same character.

Table IV shows the mean results obtained.

TABLE IV.

Anode.	Electrolyte.	No. of expts.	Current for unmagnetized steel per sq. cm.	No. of expts.	Current for N. pole.	No. of expts.	Current for S. pole.	Increase due to magnetization. N.	Increase due to magnetization. S.
Soft steel.....	5 per cent. HNO_3	7	411	4	466	3	503	55	92
Hard steel.....	5 per cent. HNO_3	12	382	6	426	6	454	44	72

Discussion.

The results presented are preliminary and are published because of the very interesting character of the phenomenon. It is our hope, by using a very much more powerful magnet and by taking pains to govern temperature and other conditions, to obtain quantitative results of greater value. In the meantime we feel that the following points are established:

1. The current density required to render nickel passive is materially increased when in the magnetic field, as was shown to be the case with iron.

2. Steel when magnetized is more difficult to render passive than is the same steel unmagnetized and soft steel is affected to a greater extent than hard steel. This accords with the observations of Andrews.[1]

3. The positive pole of the magnets is more easily rendered passive than is the negative pole.

The cause of these magnetic effects in no way appears to be indicated by the experiments and we shall have no hypothesis to offer until many more facts have been determined.

UNIVERSITY OF WASHINGTON,
SEATTLE, WASH.

NOTES.

Photosensitiv Antimonite Cells.—The fact that natural sulfide of antimony shows a very strong alteration of its electrical conductivity under the influence of light-radiation was discovered in 1907 by F. M. Jaeger.[2]

[1] *Proc. Roy. Soc., London*, 49, 489 (1893).

[2] *Proc. Royal. Acad. Sci. Amsterdam*, 9, 808 (1907). *Z. kryst. Min.*, 44, 45 (1908).

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As the so-called "inertia" of this substance after radiation was shown to be much smaller than in the case of selenium, and as also the maximum effect was obtained in quite another part of the spectrum than with the mentioned element, I thought it would be of considerable importance to construct an antimonite-cell of high sensitiveness for practical purposes. After many attempts I was led to the following method of construction: Cleaving a crystal of natural antimonite, a lamella was obtained of about 0.3 mm. thickness. This lamella was pressed against an electrode plate of glass, covered with a large number of very fine electrodes made of gold or platinum foil of 0.001 mm. thickness. These have the shape of a grate, whose small bars are distant from each other by about 0.067 mm. The width of the grate was commonly 3×4 mm., thus having about 14 electrodes per sq. mm. The required pressure on the lamella is exerted by means of a small screw-press, into the frame of which insulated wires are fitted. These wires end in small elastic bars which pinch the electrode-plate and make metallic contact with the wires of the grate.

Such cells have a resistance which varies between 10^5 and 5×10^6 ohms. A very small oil-lamp placed in the immediate neighborhood of the cell decreases this resistance to 0.1 or even 0.01 of the original value. During the passage of the current the cells are extremely sensitiv to atmospheric influences. It is therefore necessary to enclose them in vaseline, as they would otherwise be spoiled in a short time, ranging from 10 seconds to 2 hours, depending upon the current density used. A potential difference of 30 volts can be used without any trouble; but one of about 150 volts after half an hour sometimes causes the resistance to increase very rapidly, until the cells get out of order. Without too high voltages, however, they seem to last indefinitly. Although there seems to be no doubt whatever about the fact that the phenomenon depends on a change in the surface-layer of the mineral, many peculiarities have been observed which are yet to be explained, such for instance as the relations between sensitiveness and thickness of the lamella or the distance of the electrodes.[1]

For the valuable assistance, which Professor F. M. Jaeger has given me during the construction of these cells, I wish to express my best thanks.

WILLIAM SEBASTIAN GRIPENBERG.

MASABY, FINLAND, September 15, 1911.

Oxidation of Arsenious and Antimonious Oxides.—In the course of some work, having for its object the preparation of certain new organic arsenic and antimony compounds, it was found that the lower oxides of these

[1] The author is prepared to furnish cells of the kind here described. Address W. S. Gripenberg, Masaby, Finland, Europe.

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two elements are converted by air into the pentoxides, much more readily than was to be expected from the statements in the literature.

The experiments were made by dissolving the organic compound in dilute alcohol, adding the arsenious or antimonious oxide and boiling the mixture for a number of hours, in a reflux apparatus. The condenser employed consisted of an ordinary quill tube, about 18 inches in length. At the completion of the experiment the liquid always possessed a distinct odor of alcohol. The oxides were employed in varying proportion and the presence of the organic compounds, other than alcohol, appeared to exert little if any effect on the results. Arsenious oxide (0.5 gram), after being boiled during 26.5 hours, with 95 per cent. alcohol (3 cc.) and water (5 cc.), was found to have been converted completely into arsenic acid. Similar results were obtained with antimonious oxide.

It is, perhaps, hardly necessary to say that the arsenious and antimonious oxides employed were free from the higher oxides. The experiments described in this note were carried out, at my suggestion, by Mr. Volney A. Ray.

J. BISHOP TINGLE.

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CHAMPACA OIL.

BY BENJAMIN T. BROOKS.

Received August 12, 1911.

From time to time small samples of so-called champaca oil have reached Europe but in most cases these samples have had an uncertain origin and, moreover, European chemists have never had a sufficient quantity of the oil for thorough investigation.

True champaca oil, prepared from the flowers of *Michelia champaca* L., should not be confused with "champaca wood oil," distilled from the wood of *Bulnesia sarmienta* Lor. The sesquiterpene alcohol champacol, or guaiol, which is characteristic of the latter oil does not occur in true champaca oil.

There are at least four species of *Michelia*, which are well known in the Indo-Malay region, of which *Michelia champaca* L. is probably the best known.

Michelia champaca L. is a tree which attains a great size in certain localities. The author has seen specimens of this tree in the Royal Botanical Gardens at Peradeniya, Ceylon, which were over three feet in diameter and the curator, Mr. H. F. McMillan states that they sometimes reach even greater dimensions. With proper care the tree can be cultivated from either seed or cuttings. Marcottage is not a success with this species, though good results are thus obtained with *Michelia longifolia* L. The flowering season ordinarily lasts from the middle of June to about the middle part of October. The young trees bear flowers abundantly in

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the fourth year from seed. According to a recent bulletin of the firm Roure-Bertrand Fils[1] the perfume from Philippine champaca is stronger and sweeter than that of the Singapore, Penang, Colombo or Peradeniya flowers, apparently resembling Philippine ylang-ylang oil in this respect.

The fragrance of the white flowers of *Michelia longifolia* L. is altogether different from the flowers of "yellow champaca" or *M. champaca* L., and, as will be shown in the experimental part of this paper, the two oils have no constituents in common.

Michelia fuscata is a very small tree or shrub. According to Mr. H. F. McMillan, of Peradeniya, the flowers of this shrub are the most fragrant of any flower growing in Ceylon. At present these flowers are not available in sufficient quantity for a study of their essential oil.

Michelia nilagirica is a mountain species, the flowers of which are also fragrant but their odor is not as delicate as champaca.

Schimmel & Company[2] reported benzoic acid as occurring in a sample of champaca oil examined by them, but from the rest of their description this sample probably contained ylang-ylang oil. In 1907 the same chemists[3] described a champaca oil which was stated to have been prepared by distilling a mixture of the white (*M. longifolia*) and the yellow flowers (*M. champaca*). This oil contained linalool to the extent of 60 per cent. It also contained methyleugenol and an ester of methylethylacetic acid. I have found these substances in the oil from "white champaca" but altogether absent from the essential oil of the yellow flowers.

Bacon[4] recently examined an authentic oil prepared in Manila from champaca flowers and showed the presence of isoeugenol, to the extent of 3 per cent. of the oil.

In the oil prepared from champaca flowers, yield 0.37 per cent., I have shown the presence of phenylethyl alcohol, cineole, isoeugenol, benzyl alcohol, benzaldehyde, benzoic and acetic acids. The oil is fluorescent, probably owing to the presence of a small quantity of methylanthranilate.

The constants of two specimens of the oil are as follows:

	I.	II.
Specific gravity $\frac{30^\circ}{30^\circ}$	0.9040	0.9107
Refractive index, $\frac{30^\circ}{D}$	1.4640	1.4688
Ester number	124.0	146.0
Ester number after acetylating	....	199

The chemical examination of champaca oil is rendered unusually difficult by the ease with which the oil resinifies. Treatment with sodium bisulfite slightly diminishes the tendency to form resin.

[1] *Bulletin of Roure-Bertrand Fils*, 1, 26 (1909).
[2] *Semi-annual Report*, 1, 11 (1897).
[3] *Ibid.*, 2, 33 (1907).
[4] *Philipp. J. Sci.*, (*A*) 5, 257 (1910).

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The two most important constituents of champaca oil thus far determined are phenylethyl alcohol and cineole. The fine quality of champaca perfume is due largely to the presence of phenylethyl alcohol, which occurs both free and as an ester.

The importance of this alcohol in German oil of roses has recently been shown by Walbaum and Stephan[1] and Soden and Rojahn.[2] Benzoic acid and benzaldehyde are apparently only minor constituents and may result from the oxidation of benzyl alcohol, since an energetic oxidizing enzyme is present in the flowers. The presence of this oxidase also makes it quite probable that traces of the highly aromatic aldehyde, phenylacetaldehyde, are also present in the oil. Walbaum and Stephan conclude that traces of this aldehyde are present in German rose oil.

On standing, champaca oil deposits a comparatively large amount of a crystallin compound melting at 165–166°. This substance is a ketone. The presence of the oxidation products of benzyl alcohol and the crystallin ketone in champaca flowers, together with the oxidizing enzyme, is of some theoretical interest as showing how aldehydes, ketones and other oxidation products, found in many essential oils, may be formed. The tendency of benzyl alcohol slowly to form benzaldehyde by oxidation in the air is well-known but its oxidation almost certainly would be accelerated by an oxidase such as occurs in champaca flowers. Thus valerian root[3] and vanilla[4] owe the development of their characteristic odoriferous compounds to the activity of oxidizing enzymes. Work by the author with Dr. Arthur Koch, in Göttingen, now in the course of completion, has shown the presence of oxidizing enzymes in many other plants yielding essential oils which contain large per cents. of aldehydes or ketones.

The crystallin ketone in champaca flowers was first studied by Bacon[5] who showed that its empirical formula is $C_{16}H_{20}O_5$ and that it forms a crystallin phenylhydrazone and semicarbazone.

The substance is optically active. In alcohol solution it shows the rotation $[\alpha]^{30°}_{D} = -82.5°$. The compound reacts quantitatively with two molecules of sodium hydrogen sulfite forming a sulfonic acid salt, from which it is impossible to regenerate the original ketone in the usual manner. Since Knoevenagel has shown this behavior to be a property of the group —HC=CH—CO it may be concluded that this group is present in the champaca ketone.

The ketone reacts with one molecule only of phenylhydrazine forming a beautiful, crystallin phenylhydrazone having the formula $C_{16}H_{20}O_4$ =

[1] *Ber.*, 33, 2304 (1900).
[2] *Ibid.*, 33, 1720 (1900).
[3] Carle, *J. Pharm.*, [4] 12, 148.
[4] Lecomte, *Compt. rend.*, 133, 745.
[5] *Philipp. J. Sci.*, (*A*) 5, 257 (1910).

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$N.NHC_6H_5$ and melting sharply at 161°. No hydroxyl groups are present. The remaining four oxygen atoms in the molecule are bound as an ester of succinic acid. One carboxyl group of the latter is combined as the ethyl ester and the other is bound to a hypothetical ketone alcohol, which according to the empirical formula given by Bacon must be $C_{10}H_{12}O_2$. All attempts to obtain this latter compound, by splitting the molecule, were in vain, resulting under the most favorable conditions, in a light yellow oil having an odor somewhat resembling carvone, which polymerized in a few minutes to a stiff, glassy resin. As shown by Bacon the ketone itself polymerizes with great ease, particularly when gently warmed in solution in benzene. The ease with which resinification takes place in champaca oil itself, suggests the presence of structurally related compounds.

Since the substances isolated by me from the essential oil of *Michelia champaca* L. are entirely different from those isolated by Schimmel & Company[1] from oil distilled from the yellow and white flowers, a study of the oil prepared from the latter flowers has been made. The same compounds were identified in this oil as Schimmel & Company found in the champaca oil studied by them, namely linalool, the methyl or ethyl ester of methylethylacetic acid and methyleugenol. This oil showed no fluorescence at all. This property in Schimmel's oil was perhaps due to the presence of some of the oil from the yellow flowers. Extraction of the white flowers yields none of the crystallin ketone obtained from the yellow flowers.

This oil possesses an intensely sweet, fruity odor which is altogether different from the fragrance of the yellow flowers. Its constants are as follows:

Specific gravity $\frac{30°}{30°}$	0.897
Ester number	180
Refractive index	1.4470

The oil was too dark for a polariscope reading to be taken. The low refractive index is undoubtedly caused by the methylethylacetic ester.

The white flowers also contain an energetic oxidizing enzyme.

Experimental.[2]

The rapidity with which champaca flowers darken in color after picking, particularly if they are slightly bruised, is much like the behavior of gardenia flowers in this respect. According to Bertrand the latter flowers contain an oxidizing enzyme similar to laccase. Champaca flowers were therefore investigated for oxidases. When the flowers are

[1] *Loc. cit.*

[2] Some of the experiments are here only briefly outlined as they are given in more detail in a recent article by the author on Philippine essential oils, *Philipp. J. Sci.*, (*A*) 6 (1911).

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bruised under water an aqueous solution is obtained, which begins to turn brown the instant it is exposed to the air, the color gradually extending deeper into the solution. By preparing the aqueous extract under a layer of ligroin or paraffin oil a light yellow solution is obtained, which turns tincture of guaiac resin blue directly. Since this is a rather common property of plant extracts, the color reaction with α-naphthol and p-phenylenediamine was tried and positive results obtained. By heating the solution a few minutes on a steam bath the activity of the enzyme is entirely destroyed, none of the color reactions being given by the heated extract.

The oil was examined for aldehydes by shaking out with sodium bisulfite in the usual manner. From 40 grams of oil, one year old at the time of investigation, 2.1 grams of oil were extracted by bisulfite. When treated in very dilute alcohol solution with phenylhydrazine this portion gave a small quantity of crystallin benzaldehyde phenylhydrazone, which after recrystallizing from methyl alcohol melted at 154–156°. The greater part of this aldehyde fraction consisted of an oil having an odor closely resembling methylheptenone. The semicarbazones were not separated in a state of purity sufficient for positive identification of the latter compound.

Walbaum and Stephan have shown that phenylethyl alcohol is quite soluble in 30 per cent. alcohol, and since the presence of this aromatic compound was suspected in champaca oil the method proposed by them was followed. As it was desirable to know whether or not a comparatively large amount of the free alcohol was present in the original oil, 40 grams of champaca oil, previously extracted with bisulfite, were shaken out with 250 cc. of 30 per cent. ethyl alcohol. Most of the ethyl alcohol was distilled from the extract, using a condensing column, and the remaining mixture extracted with ether. In this way 2.6 grams of oil were obtained, which had a very sweet, agreeable odor and when two drops were acetylated with acetyl chloride and subsequently washed with a little sodium carbonate solution, the characteristic rose fragrance of phenylethylacetate was produced. The remaining oil was therefore dried in a little ether with potassium carbonate, and distilled. About 1.8 grams distilled between 215° and 225°, the boiling point of pure phenylethyl alcohol being 220°. This fraction was treated with phenylisocyanate and the characteristic phenylurethane of phenylethyl alcohol was obtained, which after recrystallizing from methyl alcohol melted sharply at 79.5°. Free phenylethyl alcohol is therefore present in champaca oil.

Attempts were made, with small quantities of the oil, to distil it with steam and also in a vacuum of 18 mm. but in each case a large part of the oil was converted into resin.

Therefore 75 grams of oil, which had been treated with bisulfite to

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remove all aldehydes, were treated with a slight excess of potassium hydroxide in aldehyde-free ethyl alcohol and the solution allowed to stand 24 hours. Part of the alcohol was then distilled *in vacuo*, the alkaline solution largely diluted with water, *slightly* acidified with sulfuric acid and the mixture extracted six times with petroleum ether. After distilling the petroleum ether, the resulting oil was distilled with steam. In this experiment 25 grams of oil were recovered. In other saponifications with small amounts of oil a *larger* per cent. of the oil was resinified. The viscous, resinous matter obtained by me is apparently identical with the viscous acid mixture obtained by Bacon,[1] who was unable to distil anything from it without decomposition, even *in vacuo*.

The oil, purified by distillation with steam, was shaken out with 3 per cent. sodium hydroxide, the alkaline solution slightly acidified and extracted with ether. The phenol thus obtained, weight 1.4 grams, smelled strongly of isoeugenol. Its benzoyl compound melted at 103°.

After removal of the phenol the oil was distilled at ordinary pressure up to 220°. The fraction boiling from 173 to 178° consisted of almost pure cineole, which compound was identified by making the characteristic compound with iodole, melting point 112°.

When a few drops of an essential oil are shaken up with a little hot water the odor of the more volatil constituents becomes much more pronounced. In the case of champaca oil the odor of cineole becomes quite strong when treated in this way. In my opinion cineole is one of the compounds which give to champaca its peculiar character.

The presence of a relatively small amount of benzyl alcohol was shown by oxidizing 0.5 gram of the fraction boiling from 200 to 210° with a little chromic acid mixture, distilling a little of the solution and precipitating benzaldehyde phenylhydrazone from the aqueous distillate. No evidence that linalool was present in this fraction was obtained. A small portion boiling from 198 to 200° gave no citral on oxidation. All the fractions between the cineole and phenylethyl alcohol fractions were quite small.

The fraction boiling from 210 to 220° was examined for phenylethyl alcohol as before. Acetylating a few drops gave the odor of aromatic phenylethyl acetate and oxidation of 2.0 grams with a small quantity of chromic acid mixture gave phenylacetic acid, which after crystallizing from dilute methyl alcohol melted sharply at 76°. Phenylethyl alcohol is therefore present in champaca oil as an ester and in the free state.

The aqueous acid solution was neutralized, concentrated and acidified with dilute sulfuric acid. Extraction with ether gave 0.5 gram benzoic acid, which after recrystallizing from hot dilute alcohol melted sharply at 120°. Distilling the aqueous solution with steam gave acetic acid,

[1] *Loc. cit.*

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identified by making the silver salt from the neutralized, concentrated distillate. Analysis of the silver salt gave 64.5 per cent. silver; calculated for silver acetate, 64.4 per cent.

The Essential Oil from Michelia longifolia.

Schimmel & Company[1] state that the oil sent to them in 1907 was obtained by distillation in a yield of 0.0125 per cent. By extracting the white flowers with a suitable solvent and removing the oil from the essence concrete with dilute alcohol, a yield of approximately 0.08 per cent. was obtained. Thus prepared, the oil was dark green in color and showed no fluorescence.

Twenty grams of this oil were saponified by a slight excess of caustic potash in aldehyde-free alcohol. Considerable resin was formed in this case, also. A neutral fraction weighing 9.3 grams was obtained, which was distilled at 16 mm. pressure. The following fractions were obtained: 80–90°, 3.8 grams; 90–98°, 2.0 grams; 98–110°, 1.0 gram; residue, 1.0 gram. The first and second fractions were united and treated with phthalic anhydride in benzene but no primary alcohols were obtained. Since the odor of the fraction was very suggestive of linalool it was oxidized with chromic acid mixture to citral, which was identified by making its α-naphthocinchonic acid compound, melting point 198–199°. The third fraction appeared to consist of a mixture of the second and fourth fractions. The fourth fraction, weight 1.0 gram, had a specific gravity of about 1.09 and showed the refractive index $n_D^{30°} = 1.5130$. Its odor was very suggestive of methyleugenol. Oxidation with potassium permanganate in the cold gave about 0.15 gram of veratric acid, melting point 179–180°.

No phenolic substances were identified with certainty although a trace of a phenolic substance is present, the odor of which closely resembled thymol.

After all the neutral and phenolic substances had been removed from the original solution it was concentrated to about 15 cc., acidified with dilute sulfuric acid and extracted with ether. The acids thus extracted were neutralized with a dilute sodium carbonate solution, purified by adding a little calcium acetate, filtered and the silver salt precipitated from the filtrate. The silver salt thus obtained gave on analysis 52.0 per cent. silver; calculated for $C_5H_9O_2Ag$, 51.4 per cent. The odor of the original oil is almost entirely due to the methyl or ethyl ester of this acid.

Champaca Ketone.

The crystallin ketone which is deposited by champaca oil is best purified by recrystallization from chloroform and ligroin. When quite pure it is entirely odorless and colorless. An alcoholic solution of the

[1] *Semi-annual Report*, 2, 33 (1907).

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compound deposits large, four-sided plates, the acute angles of which are 64°. The crystals possess two optical extinctions parallel to the axes of symmetry. A solution of the substance in chloroform yields large, six-sided plates, while precipitation with ligroin or ether yields the shortened, four-sided plates.

One gram of the ketone dissolved in 15 cc. of alcohol showed in a 10 cc. tube an optical rotation of —5.5°, $[\alpha]_D = 82.5°$.

The substance melts at 165–166°, but polymerizes rapidly at this temperature, yielding an amorphous substance which melts with decomposition at 335–340°. About 0.3 gram of the pure ketone was heated in an oil bath at 170° until thoroughly softened. After cooling, the addition of chloroform readily extracted the unchanged substance, which could be recrystallized. There remained about 0.2 gram of insoluble amorphous material, which could not be dissolved, the substance slowly absorbing the solvent and thereby being converted into a tough, gelatinous mass.

Twenty grams of the ketone were dissolved in a mixture of benzene and alcohol and shaken in a shaking machine for 4 hours with a concentrated solution of sodium bisulfite. At the end of this time the benzene layer was evaporated and 0.2 gram amorphous substance was obtained. The ketone had therefore passed quantitatively into the bisulfite solution. On treating the bisulfite solution with sodium carbonate, nothing separated, even on warming, as is usually the case. A small test portion yielded nothing on making strongly alkaline with sodium hydroxide. Extraction of the alkaline solution with chloroform yielded nothing.

When the neutralized, aqueous sulfite solution was evaporated on the steam bath, a heavy viscous layer finally separated from the concentrated solution. This substance was very soluble in water. On standing several days *in vacuo* over sulfuric acid it slowly crystallized. On ignition it burned with a smoky flame leaving a residue of sodium sulfite and sulfate. It was not obtained sufficiently pure for analysis. The aqueous solution, slightly acidified with acetic acid, gives no precipitate with phenylhydrazine. What was apparently the free sulfonic acid was prepared, in a very small yield only, by digesting a few grams of the salt with glacial acetic acid. This mixture was extracted with chloroform yielding an oily, acid substance totally different from the original material.

The ketone reacts with one molecule only of phenylhydrazine. The resulting phenylhydrazone, melting sharply at 161°, gave the following analysis; 0.2057 gram substance gave 14.2 cc. of nitrogen measured at 30° and 760 mm. Calculated for $C_{16}H_{20}O_4 : N.NH.C_6H_5$, 7.33 per cent. nitrogen; found, 7.48 per cent. nitrogen.

Only one double bond is reactive to Hanus' iodine solution, although more than one is undoubtedly present. 0.2035 gram of the ketone absorbed 0.171 gram iodine; calculated for one double bond, 0.176 gram

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iodine. The double bond in the group —HC=CH—CO—, indicated by the reaction with bisulfite, is very reactive and is probably the one which reacts in this instance.

A small sample of the ketone was dissolved in acetic anhydride and heated for 1 hour on the steam bath, but the original substance was recovered unchanged. Higher temperature or acetyl chloride quickly destroys the compound.

On treating the ketone with caustic potash in a strong alcoholic solution, crystals of a potassium salt soon begin to separate out in the form of masses of minute needles. The salt was filtered with suction and recrystallized from absolute alcohol with the addition of potassium ethylate. The lead salt, made by adding lead nitrate to an aqueous solution of the salt, is amorphous when first precipitated, changing in the course of a few hours to crystals. Under the microscope these crystals proved to be rhombic plates, the acute angles of which measured approximately 72°. The lead salt decomposed with almost explosive violence when combustion analyses were attempted. Two lead determinations gave 65.2 and 65.4 per cent. of lead. Fully neutralized lead succinate should contain 64.0 per cent. of lead but according to Beilstein[1] it is slightly basic in composition when precipitated from a neutral solution. The salt is therefore lead succinate.

The odor evolved when 0.5 gram of the original material is treated with a little alcohol, fused zinc chloride and a few drops of hydrochloric acid is apparently identical with the odor of diethyl succinate.

Saponification of 10 grams of the ketone and distillation of a portion of the mixture yielded ethyl alcohol. The iodoform reaction gave iodoform, slowly at 30° and very quickly at 60°.

Summary.

The differences between the essential oils of *Michelia champaca* L. and *Michelia longifolia* L. are clearly shown. The value of champaca oil is largely due to the presence of phenylethyl alcohol and its esters. The most characteristic compound in the oil from the flowers of *Michelia longifolia* L. is the methyl or ethyl ester of methylethyl acetic acid. An unstable ketone separates from champaca oil, which has been shown to be the succinic acid ester of a ketone alcohol and ethyl alcohol. The ketone alcohol probably has the formula $C_{10}H_{12}O_2$ and contains the group —HC=CH—CO—. The flowers of both species studied contain an oxidizing enzyme. It is believed that such oxidizing enzymes play an important role in the formation of aldehydes and ketones in essential oils. The study of the crystallin ketone will be continued.

I desire to express my thanks to Dr. Carlos Jährling, of Manila, for many

[1] Beilstein, *Org. Chemie*, 1; 655.

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helpful suggestions and much encouragement during the course of the investigation.

GÖTTINGEN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE OXIDATION OF METANITROBENZOYLFORMALDEHYDE.

BY WILLIAM LLOYD EVANS AND EDGAR JOHN WITZEMANN.

Received September 9, 1911.

In a previous report on the preparation and the oxidation of *m*-nitrobenzoylcarbinol[1] it was indicated that a study would be made of some of the substituted benzoyl carbinols for the following purposes: (1) to ascertain whether the same general course of reaction is followed as has been previously developed for this series of compounds[2] and (2) to discover what possible effect, if any, the introduction of substituents into the ring might have on these compounds towards oxidizing agents previously considered. This paper, which constitutes the second report on this work, deals solely with the preparation and the oxidation of *m*-nitrobenzoylformaldehyde. Briefly, the results of our experiments are as follows: (1) *m*-nitrobenzoylformaldehyde can be isolated as an actual oxidation product from *m*-nitrobenzoyl carbinol by means of copper acetate; (2) *m*-nitrobenzoylformaldehyde with potassium permanganate, potassium permanganate and sodium hydroxide, potassium ferricyanide and sodium hydroxide, freshly precipitated silver oxide and sodium hydroxide, freshly precipitated mercuric oxide and sodium hydroxide, yields *m*-nitrobenzoic acid exclusively; (3) both freshly precipitated silver oxide and mercuric oxide in the absence of an alkali were not reduced at room temperature by *m*-nitrobenzoylformaldehyde; (4) at 100° both of the reagents mentioned in (3) reacted in the same manner as the reagents in (2), *i. e.*, to give *m*-nitrobenzoic acid; (5) *m*-nitrobenzoylformaldehyde with hot aqueous solutions of copper acetate undergoes the benzilic acid rearrangement giving *m*-nitromandelic acid; (6) with alkalies the aldedyde undergoes the same rearrangement.[3] From the experiments on *m*-nitrobenzoyl carbinol previously reported and also from those herein given, the following conclusions may be drawn: (1) *m*-nitrobenzoyl carbinol and *m*-nitrobenzoylformaldehyde follow the same general course of reaction as the corresponding non-substituted compounds; (2) the two nitro-substituted compounds are more sensitive to reagents in the presence of alkalies; (3) there is a more general tendency for the oxidation reactions to progress to the benzoic acid (*i. e.*, *m*-nitrobenzoic acid) stage in the case of the two nitro-substituted compounds rather

[1] Evans and Brooks, THIS JOURNAL, 30, 404.

[2] Evans, *Am. Chem. J.*, 35, 115.

[3] Nef, *Ann.*, 335, 271, 272; 357, 215, 231, 299, 302, 305, 308, 309.

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than to give the possible intermediate substances, *i. e.*, *m*-nitromandelic acid and *m*-nitrobenzoylformic acid.

Experimental Part.

Preparation of m-Nitrobenzoylformaldehyde. (a) *m-Nitrobenzoylcarbinol and Copper Acetate.*—It has previously been shown[1] that benzoyl carbinol, when subjected to the mild oxidizing action of cold aqueous solutions of copper acetate and also copper sulfate, yields benzoylformaldehyde-monohydrate, which is identical in every respect with the synthetic substance obtained by Von Pechman.[2] In some preliminary experiments made previously[3] on the action of copper salts on *m*-nitrobenzoyl carbinol, an oil was obtained which did not react with Fehling's solution even after prolonged boiling, and which, with phenylhydrazine, gave a beautiful yellowish red crystalline product. These experiments have been repeated as follows: to three grams of *m*-nitrobenzoyl carbinol (1 mol.) dissolved in 300 cc. of water was slowly added a solution of 9 grams (3 mols.) of copper acetate dissolved in 150 cc. of water. The reaction mixture became turbid immediately and in the course of 30 minutes a considerable quantity of cuprous oxide had separated out. After having stood two weeks at room temperature to ensure completeness of reaction, the yield of red cuprous oxide was found to be 1.3 grams (theory = 1.17 grams). The ether solution, which was obtained by extracting the filtrate from the cuprous oxide 12 times with ether and drying the same with sodium sulfate, yielded a thick, viscous, straw-yellow oil having the mild characteristic odor of benzoylformaldehyde monohydrate. In order to remove the acetic acid present, the oily residue was dissolved in 25 cc. of water and the resulting solution was then treated with one gram of calcium carbonate. After having stood 12 hours with frequent stirring, the aqueous filtrate from the calcium carbonate was extracted with ether five times, the moist ether extract after drying as above yielding 2.7 grams of *m*-nitrobenzoylformaldehyde (theory = 2.96 grams).

(b) *ω-Monobromo-m-nitroacetophenone.*—To 10 grams of ω-monobromo-*m*-nitroacetophenone suspended in 500 cc. of water were added 6.9 grams (1 mol.) of silver nitrate. After boiling the mixture for two hours under a reverse condenser, the silver bromide was filtered off, the filtrate being immediately treated with calcium carbonate as in the preceding experiment. After extracting with ether and drying, a yield of 6.0 grams (theory 7.3 grams) of *m*-nitrobenzoylformaldehyde was obtained. It was found that by long-continued boiling an increasing amount of *m*-nitrobenzoic acid was produced. The same general results were obtained by the use of lead nitrate instead of silver nitrate.

[1] *Am. Chem. J.*, 35, 121–123.
[2] *Ber.*, 22, 2557.
[3] Evans and Brooks, THIS JOURNAL, 30, 408.

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Properties of m-Nitrobenzoylformaldehyde.—*m*-Nitrobenzoylformaldehyde as obtained in these experiments is a straw-yellow, slow-flowing oil. On long standing it becomes more viscous until it seems to be almost solid. After standing for four months, a sample of the most carefully prepared specimen did not exhibit the slightest tendency to crystallize. This property is identical with the dehydrated benzoylformaldehyde described by Von Pechmann.[1] Numerous attempts were made to crystallize the substance from the usual organic solvents and mixtures of them but without success. *m*-Nitrobenzoylformaldehyde does not form a monohydrate, nor can it be distilled without decomposition even at reduced pressure. It does not reduce Fehling's solution or ammoniacal silver nitrate solution.

Identification of m-Nitrobenzoylformaldehyde.—Owing to the extremely viscous nature of *m*-nitrobenzoylformaldehyde it was found inconvenient to analyze it. The two following methods were employed in its identification: (1) by converting it into the osazone and comparing this with the osazone formed from *m*-nitrobenzoylcarbinol; and (2) by converting it into *m*-nitromandelic acid. It was found most convenient to handle the substance for measurement in an ether solution, the oily residue obtained therefrom being dissolved subsequently in water.

(a) *Preparation of m-Nitrobenzoylformaldehyde Osazone from m-Nitrobenzoyl Carbinol.*—The method employed was an adaptation of Laubmann's method[2] for preparing the osazone of benzoyl carbinol, except that the *m*-nitrobenzoyl carbinol was used instead of previously preparing the hydrazone. A solution of one gram of *m*-nitrobenzoyl carbinol in the minimum amount of warm 50 per cent. alcohol was added to a warm concentrated solution of 4 grams of phenylhydrazine hydrochloride and 5 grams of fused sodium acetate in 50 per cent. alcohol, the reaction mixture being immediately heated in a sealed tube for four hours at 100°. The weight of the beautiful dark red needle-like crystals (which filled the tube), on allowing the tube to cool in the furnace over night after washing with 50 per cent. alcohol and drying, was 1.2 grams. This substance, after crystallizing three times from boiling benzene, gave a sharp melting point of 223° and analyzed as follows:

Calculated for $C_{20}H_{21}N_5O_2$: C, 66.98; H, 4.50; N, 19.59
Found: C, 66.45; H, 4.90; N, 19.74, 19.56

(b) *Preparation of m-Nitrobenzoylformaldehyde Osazone from m-Nitrobenzoylformaldehyde.*—One gram of *m*-nitrobenzoylformaldehyde, prepared by the action of copper acetate on *m*-nitrobenzoyl carbinol as described above, was dissolved in 25 cc. of water and to this solution 3 grams of phenylhydrazine were added. The dark-red oil, which was formed

[1] *Loc. cit.*

[2] *Ann.*, 243, 246.

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at first, was converted to a friable chalk-like mass on continued heating. This substance, when purified as in the preceding experiment, was found to be identical in every respect with the osazone obtained by the reaction of *m*-nitrobenzoyl carbinol and phenylhydrazine. The procedure described in this experiment was repeated on the oils obtained by the reaction of silver and lead nitrates on ω-monobromo-*m*-nitroacetophenone, the result in each case being an osazone identical with the one described. Two and one-half grams of a neutral oil obtained from the action of aqueous copper sulfate on three grams of *m*-nitrobenzoyl carbinol yielded with 3.00 grams of phenylhydrazine by this method a product which was identical in every respect with the osazone above described. These experiments prove, therefore, the identity of these oils to be *m*-nitrobenzoylformaldehyde.

m-Nitromandelic Acid from m-Nitrobenzoylformaldehyde.—(*a*) As is well known benzoylformaldehyde undergoes the benzilic acid rearrangement when acted on by aqueous solutions of the alkalies[1] and also of copper salts at 100°[2] forming *dl*-mandelic acid. As is shown above, *m*-nitrobenzoyl carbinol with copper acetate at ordinary temperature gives *m*-nitrobenzoylformaldehyde. Owing to its extreme sensitiveness towards caustic alkalies, the simultaneous formation of *m*-nitrobenzoylformaldehyde and its rearrangement were accomplished by a study of the behavior of *m*-nitrobenzoyl carbinol towards copper acetate at 100°. To a solution of two grams of *m*-nitrobenzoyl carbinol in 300 cc. of water was added a solution of 8.64 grams of copper acetate dissolved in 250 cc. of water. The reaction mixture, which showed almost immediately by its change of color that reduction was taking place, was heated to boiling for four hours. The residue, consisting of cuprous oxide and copper *m*-nitromandelate, weighed 3.38 grams. The filtrate, which was obtained by boiling this residue for some time with water, showed no reaction with ammonium hydroxide, thus showing the insolubility of copper *m*-nitromandelate and the absence of copper acetate. In order to obtain the weight of the copper *m*-nitromandelate, it was found most convenient to remove the cuprous oxide from the residue by levigation and finally 2.12 grams (theory = 2.50 grams) of the salt and 1.10 grams of the red cuprous oxide were obtained. The solution which was obtained by dissolving the salt in 70 cc. of dilute hydrochloric acid (1 : 3.33) was extracted with ether 6 times. The combined ether extracts after drying yielded 1.73 grams (theory = 1.84 grams) *m*-nitromandelic acid (m. p. = 118°). The amount of *m*-nitromandelic acid demanded by theory from the amount of *m*-nitrobenzoyl carbinol used was 2.17 grams, the amount obtained being therefore 80 per cent. From these results it was expected

[1] Von Pechmann, *Ber.*, 22, 2557. Evans, *Am. Chem. J.*, 35, 122.
[2] *Am. Chem. J.*, 35, 124.

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that *m*-nitromandelic acid would react with copper acetate to form an insoluble copper salt. One gram of crystallized copper acetate dissolved in 25 cc. of water was added to a solution of one gram of *m*-nitromandelic acid in 25 cc. of water. The green salt, which began to separate almost immediately in the cold and was subsequently separated completely by boiling for 2.5 hours, was identical with the one found by the action of copper acetate and *m*-nitrobenzoylcarbinol. Yield = 1.14 grams (theory = 1.15 grams).

(*b*) When *m*-nitrobenzoylformaldehyde was tested with caustic alkalies it yielded *m*-nitromandelic acid which contained varying amounts of *m*-nitrobenzoic acid. This same behavior has been previously noted with lime and benzoylformaldehyde.[1] A solution of three grams of *m*-nitrobenzoylformaldehyde in 75 cc. of water was made slightly alkaline with 1.2 grams of sodium hydroxide. When this reaction mixture was worked up in the usual way, 2.05 grams of a yellow oil were obtained, which solidified on the addition of a trace of pure *m*-nitromandelic acid. For the reason above stated, the melting point was found to be 111°–113°, which was raised by the addition of the pure compound.

The Oxidation of *m*-Nitrobenzoylformaldehyde.

m-Nitrobenzoylformaldehyde and Potassium Permanganate.—When benzoylformaldehyde is oxidized by potassium permanganate, benzoic acid is formed exclusively, while in the presence of alkalies benzoylformic and benzoic acids are formed.[2] The substituted aldehyde gives *m*-nitrobenzoic acid exclusively with potassium permanganate alone, and also in the presence of sodium hydroxide as is shown by the following experiments. A solution of 4.44 grams (3 mols.) of potassium permanganate, dissolved in least amount of water, was added to 1.57 grams (1 mol.) of *m*-nitrobenzoylformaldehyde dissolved in 250 cc. of water. With very gentle warming and frequent shaking of the mixture for 24 hours, reducing the excess of potassium permanganate with a few drops of ethyl alcohol, and working up in the usual way, a yield of 0.87 gram (theory = 1.4 grams) of *m*-nitrobenzoic acid was obtained. Since *m*-nitrobenzoylformic acid and *m*-nitromandelic acid give *m*-nitrobenzoic acid exclusively when treated with sodium hydroxide and potassium permanganate,[3] it was expected that *m*-nitrobenzoylformaldehyde would yield the same product. That this proved to be the case was shown as follows: To 1.56 grams (1 mol.) of *m*-nitrobenzoylformaldehyde in 250 cc. of water was added a mixture of 2.76 grams (2 mols.) of potassium permanganate and 0.70 gram (2 mols.) of sodium hydroxide. The reaction mixture, after standing at room temperature for 48 hours, yielded 0.94 gram (theory = 1.39 grams)

[1] *Am. Chem. J.*, 35, 123.
[2] *Ibid.*, 35, 128, 129.
[3] THIS JOURNAL, 30, 409.

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of *m*-nitrobenzoic acid. Owing to the extreme sensitiveness of the aldehyde towards reagents (see above), slight amounts of tar were formed in these two experiments.

m-Nitrobenzoylformaldehyde, Potassium Ferricyanide and Potassium Hydroxide.—In striking contrast to the behavior of benzoyl carbinol and benzoylformaldehyde towards alkaline potassium ferricyanide[1] is that of *m*-nitrobenzoylcarbinol and *m*-nitrobenzoylformaldehyde, the non-substituted compounds giving mandelic acid while the substituted compounds give *m*-nitrobenzoic acid. To a solution of 1.63 grams (1 mol.) of *m*-nitrobenzoylformaldehyde in 200 cc. of water was added an aqueous solution of 9 grams (3 mols.) of potassium ferricyanide and 1.85 grams (5 mols.) of sodium hydroxide. After standing at room temperature, the reaction mixture yielded by the usual treatment 1.05 grams (theory = 1.58 grams) of *m*-nitrobenzoic acid.

m-Nitrobenzoylformaldehyde and Silver Oxide.—*m*-Nitrobenzoyl carbinol, when acted upon by silver oxide in the presence or absence of alkalies, gives *m*-nitrobenzoic acid, a result which is in accord with the action of the same reagents on benzoyl carbinol and the results obtained by Denis on acetol.[2] Since in the following experiments it will be shown that *m*-nitrobenzoylformaldehyde under either condition gives *m*-nitrobenzoic acid exclusively, it is perfectly evident therefore that *m*-nitrobenzoylformaldehyde, in the presence of silver oxide and sodium hydroxide, does not undergo the benzilic acid rearrangement before oxidation, but it must previously have dissociated into *m*-nitrobenzaldehyde and carbon monoxide, and these compounds then in turn were oxidized:

$$NO_2.C_6H_4.CO.CHO \longrightarrow NO_2.C_6H_4.CHO + CO$$

This interpretation of the reaction is in harmony with the results obtained by the oxidation of the corresponding carbinol, which possesses the possibility of dissociating as follows:

$$1.\ NO_2.C_6H_4.CO.CH_2OH \longrightarrow NO_2.C_6H_4.CO.CH \swarrow + HOH$$

$$2.\ NO_2.C_6H_4.CO.CH_2OH \longrightarrow NO_2.C_6H_4CHO + H_2CO$$

Thus, it is seen that in the presence of alkalies the *m*-nitrobenzoylmethylene formed in (1) possesses the possibility of being oxidized to *m*-nitrobenzoylformaldehyde, which substance would then oxidize as herein indicated.[3] It is interesting to note here that the bivalent carbon derivative in (1) possesses the possibility also of polymerizing and forming the derivatives of benzoylmethylene prepared by Paal and his students.[4] Paal interprets the formation of the tribenzoylcyclotrimethylene[5] upon the basis

[1] *Am. Chem. J.*, 35, 127.
[2] Denis, *Am. Chem. J.*, 38, 579.
[3] Compare Nef, *Ann.*, 335, 191.
[4] Paal and Schulze, *Ber.*, 33, 3784; 35, 168. Nef, *Ann.*, 335, 251.
[5] *Ber.*, 36, 2425.

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of the existence of bivalent carbon derivatives first proposed by Nef. It is apparent that in the absence of alkalies, the oxidation of *m*-nitrobenzoyl carbinol could proceed through equation (2). The freshly precipitated and well washed silver oxide obtained from 5.01 grams (2.2 mols.) of silver nitrate was added to 1.17 grams (1 mol.) of *m*-nitrobenzoylformaldehyde in 200 cc. of water. No reduction having taken place after standing at room temperature for 48 hours, the reaction mixture was kept at the temperature of the boiling water-bath for several hours, whereupon reduction took place, as was evident from the deposit of metallic silver on the sides of the flask. After separating the silver oxide and soluble silver salts from the metallic silver by means of ammonium hydroxide, and working up the filtrate in the usual way, there was obtained 0.78 gram (theory = 1.11 grams) of *m*-nitrobenzoic acid.

Similarly 1.39 grams (1 mol.) in 200 cc. of water were tested with a mixture of 0.61 gram (2.1 mols.) of sodium hydroxide and the freshly precipitated and well washed silver oxide obtained from 7.18 grams (2.5 mols.) of silver nitrate. The same general phenomena were observed as in the preceding experiment. The reaction mixture yielded 0.95 gram (theory = 1.29 grams) of *m*-nitrobenzoic acid.

m-Nitrobenzoylformaldehyde and Mercuric Oxide.—Equal in interest to the preceding experiments are those with mercuric oxide alone and with sodium hydroxide. *m*-Nitrobenzoyl carbinol is analogous to benzoyl carbinol in its behavior towards these reagents, in that it gives *m*-nitrobenzoic acid exclusively. Since it is herein shown that *m*-nitrobenzoylformaldehyde does not undergo oxidation with mercuric oxide alone, it must be concluded that *m*-nitrobenzoyl carbinol in oxidizing must dissociate in the presence of this reagent as indicated in (2) above. To a solution of 1.49 grams (1 mol.) of *m*-nitrobenzoylformaldehyde in 200 cc. were added 2.23 grams (1.25 mols.) of freshly precipitated and well washed mercuric oxide. After standing at room temperature for 48 hours and finally heating for some hours on the water-bath, no reduction was observed. The reaction mixture was found to contain no *m*-nitrobenzoic acid. In the presence of alkali, the result was the same as that obtained by the use of silver oxide and sodium hydroxide. Since *m*-nitromandelic acid is unacted on by this reagent, it is obvious that the mechanism of the oxidation of the aldehyde with mercuric oxide and sodium hydroxide must be the same as with silver oxide and sodium hydroxide. To a mixture of 0.5 gram (2 mols.) of sodium hydroxide and 2.23 grams (1.25 mols.) of mercuric oxide covered with water were added 1.48 grams of *m*-nitrobenzoylformaldehyde in 200 cc. of water. Reduction took place almost immediately and the reaction went to completion without the addition of heat. The reaction mixture yielded 0.92 gram (theory = 1.16 grams) of *m*-nitrobenzoic acid. It is of considerable

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interest to note the difference in behavior of the two aromatic aldehydes herein considered, and of methyl glyoxal (pyruvic aldehyde) towards silver and mercuric oxide in the presence of sodium hydroxide. Denis[1] found that with methyl glyoxal the benzilic acid rearrangement is practically not affected by the presence of the oxide of mercury or silver, while the two aromatic aldehydes give practically no other substance than the benzoic acid. In the case of benzoylformaldehyde with silver oxide and sodium hydroxide a trace of mandelic acid was obtained[2] but the main product was an almost quantitative yield of benzoic acid. In conclusion we wish to thank Mr. Evan Mahaffey, of this laboratory, for the carbon and hydrogen determinations of the osazone analysis given above.

COLUMBUS, OHIO.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK.]

THE PREPARATION OF TRIBASIC PHENOLPHTHALATES.

BY P. A. KOBER AND J. THEODORE MARSHALL.

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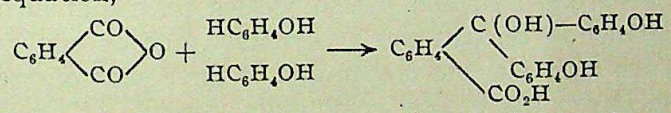
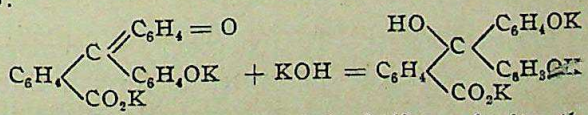
Introduction.

When Baeyer[3] heated phenol and phthalic anhydride in the presence of sulfuric acid, he did not obtain phenolphthalic acid as follows from the equation,



but obtained a substance having one molecule of water less; namely, a lactone or anhydride, which is called phenolphthalein.

Phenolphthalic acid has not yet been prepared, and according to Baeyer it does not exist. Recently the fading of the phenolphthalein color, due to excess of alkali, has been ascribed to the formation of salts of phenolphthalic acid.[4]



We determined from the study of the fading velocity, that the colorless substance was the product of one molecule of alkali and one molecule of dibasic alkali phenolphthalein.[5] On determining the concentration of the reacting substance at equilibrium, we found that the result agreed with the following equation:

[1] *Am. Chem. J.*, 38, 585.
[2] *Ibid.*, 35, 131.
[3] Baeyer, *Ber.*, 4, 659 (1874).
[4] Green and Perkin, *J. Chem. Soc.*, 85, 389. Acree, *Am. Chem. J.*, 42, 122.
[5] Kober and Marshall, THIS JOURNAL, 33, 59 (1911).

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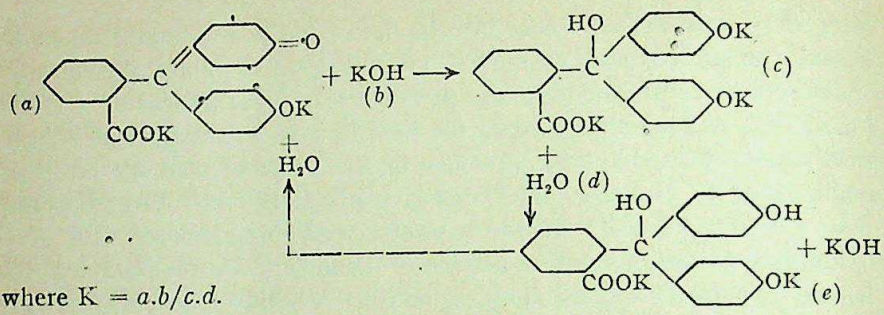

where $K = a.b/c.d.$

These experiments support the hydration theory of the formation of alkaline phenolphthalates.

In a previous paper[1] we gave the description and analysis of tripotassium phenolphthalate in order to corroborate our theoretical deductions, but did not include the method of preparation. Therefore, it is the object of this paper to give the preparation and composition of these alkaline phenolphthalates.

Preparation of Phenolphthalates.

In the early part of the work we found that the colorless salt in solution was extremely unstable, returning in the absence of alkali to the colored form very quickly. This led to the belief that it existed only in the presence of free alkali. The finding of a few colorless crystals, which on being dissolved and heated yielded phenolphthalein, showed that the isolation of the salt was a possibility, and on applying deductions from the mass law the preparation of these salts offered no particular difficulty. Using the equilibrium formula $K = a.b/c.d.$ or $c = a.b/d.K.$, we found that a strong concentration of phenolphthalein (a) together with a strong concentration of alkali (b) on one hand, and a low concentration of water (d) on the other hand, gave us the most suitable concentrations for the production of alkali phenolphthalates (c). The low concentration of water was obtained by evaporating the reaction mixture in a vacuum.

Tripotassium Phenolphthalate.—To 100 grams of commercial phenolphthalein, mixed with sufficient hot water to form a thick paste, are added 200 to 300 grams of potassium hydroxide in the form of a hot saturated solution. The resulting solution is concentrated over a steam bath in a vacuum pan at a low pressure, until the liquid is filled with crystals. In this laboratory a good water pump gave us sufficient vacuum for this purpose. A capillary tube inserted as an inlet for air to the pan, which keeps the liquid in a state of agitation, was found advantageous. Rapid evaporation, which tends to cause the formation of crystals in too minute a form, is to be avoided. Usually the crystals can be filtered through a Buchner funnel, using filter paper

[1] *Loc. cit.*

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or asbestos, but if the crystals are too small or the mother liquid too viscous, a mat of rough asbestos fiber will serve satisfactorily. Suction is applied until most of the mother liquid has been removed and the crystals are nearly dry. The purification of the crystals is accomplished by removing the crystals from the filtering apparatus to a large dish or mortar and mixing them with cold benzene or petroleum ether containing 20–30 per cent. alcohol.

After thoroughly washing the crystals in this way five or six times, the crystals can be finally washed with a small quantity of 95 per cent. ethyl alcohol cooled to —10°, followed by one washing with absolute alcohol at a low temperature. The alcohol will dissolve all of the alkali and at the same time some tribasic salt. After filtering off all of the alcohol the crystals are washed with two portions of absolute ether, and immediately dried in a vacuum desiccator. To obtain perfectly colorless crystals, the washing and drying should be done quickly and under conditions of coolness and freedom from moisture. The yield varies from 60 to 80 per cent., depending on the number of washings. We give here the analysis of the salt as stated in our first paper:[1]

Calculated for $C_{20}H_{12}O_4K_3(OH).5H_2O$:	C, 44.38; H, 4.27; K, 21.73
Found:	C, 44.40; H, 4.37; K, 21.77

The crystals, upon microscopic examination, are revealed as colorless rhomboidal plates, which rapidly assume small, discrete, superficial areas of color, giving the mass when viewed microscopically, a pinkish tint. On careful heating they lose water and their crystallin form taking on an intense opaque purple color (the dibasic salt, see salt of Meyer and Spengler[2]) with a bronze iridescence, simulating in luster crystals of potassium permanganate. They retain their purple tint on cooling in the absence of moisture, but on exposure to air fade by passing through various tones of red to lighter colors, after which they deliquesce. Under ordinary conditions, the almost colorless salt is fairly stable, showing only a slight pink tint. The crystals are insoluble in ethyl ether, benzene and acetone, slightly soluble in amyl alcohol, but in water, and also in ethyl alcohol they dissolve rapidly with the production of very little color, especially if the temperature be kept at 0°. Upon long standing or boiling the aqueous solution intense color develops.

Trisodium Phenolphthalate. — The isolation of the corresponding sodium salt involves considerable difficulties. As the sodium salt is more soluble and hydroscopic than that of potassium, it is necessary to evaporate to a greater concentration and in general to handle the product at a lower temperature. Large crystals are here very necessary for the successful isolation of the pure sodium salt.

[1] *Loc. cit.*

[2] *Ber.*, 38, 1318; 41, 2446.

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Although the general method of preparation of the sodium salt is the same as that of the potassium salt, yet the details of its preparation may be worth giving and are as follows:

One hundred and fifty grams of commercial phenolphthalein in an aqueous paste were treated with 200 grams of sodium hydroxide dissolved in the least quantity of hot water. After evaporating in a vacuum for an hour or more, large crystals filled the dish. The mother liquor was drawn off through a perforated plate with the aid of suction, and the crystals washed in turn with alcoholic benzene, alcohol and ethyl ether, at a temperature not above 0° as described under the preparation of the potassium salt. After drying, 170 grams of sodium phenolphthalate were obtained, making a yield of 63 per cent.

This process of purification of the sodium salt is not quite satisfactory; under the best of conditions the salt always contains from 0.6 to 0.7 per cent. excess of sodium, which is equivalent to 0.2 and 0.3 molecule above the required three molecules. Attempts to improve the purification by using acetone as a washing medium were unsuccessful, as a tendency of the acetone to react with the phthalates was observed similar to the action observed by Orndorff and Delbridge.[1]

On determining the amount of phenolphthalein and sodium, it was found that the results were fairly consistent with the formula

$$C_{20}H_{12}O_4Na_3(OH) + 6H_2O.$$

	Found.		Theor.
Phenolphthalein (less 2 atoms of hydrogen)	60.0	60.7	61.9
Sodium	14.2	14.1	13.5
$OH + 6H_2O$ (by difference)[2]	25.8	25.2	24.5

Trisodium phenolphthalate crystallizes in simple rhombohedrons.[3] Its properties are similar to those of the potassium salt but it is more soluble and apparently less stable.

In general these alkaline phthalates are beautiful well defined, colorless crystals, and when kept in a cool and dry place are stable for months. Of the three molecules of alkali, two are easily neutralized, even by weak acids such as acetic, carbonic, etc. The third molecule of alkali, most probably joined to the carboxyl group, is fairly resistant, but is easily

[1] Orndorff and Delbridge found that acetone readily formed a compound with tetrachlorogallein (*Am. Chem. J.*, 46, 1 (1911)).

[2] In his article on the pharmacological action of the phthalates, Rowntree (*J. Pharmacol.*, May, 1911) gives, according to our investigation, two molecules of water of crystallization to the sodium salt. This datum, which was based on an alkalinity titration, is unfortunately incorrect as it was obtained under the wrong assumption that it was, like the potassium salt, free from excess of alkali.

[3] In our first paper we give in the addendum, the crystallization of the sodium salt as cubes. Although most of the crystals are cubical in appearance, they do not belong to that system.

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displaced by mineral acids. The salts are insoluble in ethereal solvents and acetone, but are readily soluble in ethyl alcohol and water.

Summary.

(1) A description is given, for the first time, of a method for the isolation of tribasic phenolphthalates.

(2) Trisodium and tripotassium phenolphthalate are described.

We hope to apply this hydration method to other compounds, containing a phthalic acid group, such as the chloro and bromo derivatives of phenolphthalein, fluorescein, gallein, etc.

CONCERNING THE DECOMPOSITION OF URIC ACID BY MEANS OF DILUTE SODIUM HYDROXIDE SOLUTIONS.

By Clarence E. May.

Received September 13, 1911.

In recent years there have appeared in the literature three methods of biochemical importance, methods in which it seems to be the notion that by cutting down the dissociation of a given reagent, the activity of the reagent may be muzzled so that the desired action may be obtained without any side reactions taking place. The first of these methods to be proposed had to do with the determination of uric acid in urine, by the Folin-Shaffer method, wherein ammonium sulfate was added to prevent decomposition of the uric acid while precipitating the latter by means of ammonium hydroxide. In cutting down the dissociation of the ammonium hydroxide by having a large amount of ammonium sulfate present, the uric acid decomposition was diminished. The second method proposed was the Folin method for the determination of urea in urine. By having a large amount of magnesium chloride present along with the hydrochloric acid in the digestion mixture, it seemed that the dissociation of the acid was cut down and as a result the action of the acid on the non-urea constituents of urine was but slight.

Recently a modification of the Folin method for the ammonia estimation in urine was proposed by Steele[1] and in the modified method it was suggested that by the addition of a very large excess of sodium chloride it was possible to cut down the activity of the sodium hydroxide employed in the method to liberate the ammonia, since the dissociation of the caustic soda would be diminished by the presence of the sodium chloride. In other words, since the use of sodium hydroxide rather than sodium carbonate seemed necessary for the complete liberation of the ammonia in a mixture such as urine, the side action of the alkali on other urinary constituents would be prevented by the presence of an excess of sodium chloride.

[1] *J. Biol. Chem.*, 8, 365.

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In an article published recently, the present author has been engaged jointly in an investigation of the deportment of uric acid under the influence of alkalis.[1] It was noted that after exposure to the action of alkalis, uric acid disappeared, and starting with weighed quantities of uric acid, it was never possible to recover all the original acid. This disappearance of the uric acid was more or less dependent on the amount and nature of the neutral salt present in the alkaline mixture. The salts as a rule did not seem to entirely prevent the decomposition of the uric acid; they seemed to only diminish the action. In the present work it seemed desirable to study the effect of sodium hydroxide on uric acid both with and without sodium chloride present. The main point of interest was the ammonium liberated from uric acid under conditions such as the modified Folin method required for the estimation of ammonia in urine.

In the present work, the author has used solutions of uric acid in about the concentration met in normal urine, 0.25 gram uric acid to 500 cc. solution. The alkali used was pure stick caustic soda dissolved in ammonia-free, distilled water. The two concentrations of sodium hydroxide were identical with those used by Steel, namely 1.0 gram NaOH per 25 cc. and 0.5 gram NaOH per 25 cc. H_2O. Tests were carried out using no sodium chloride, tests using a reasonable amount of sodium chloride (amounting to about one-third saturated solutions) and also tests using solutions that were thoroughly saturated with sodium chloride (Kahlbaum's). Room temperature only was employed. In some cases the aërations were started at once after dissolving the acid in the alkali. Other results were obtained on aliquot portions of the same original solutions that had been allowed to stand for a day or two. During the intervals of standing, there was no agitation.

The air current employed for pulling the ammonia from the alkaline solutions was thoroughly under control at all times and the volume of air passed through amounted to about fifty liters of ammonia-free air. A demijohn of that capacity was filled with water and a ten-foot column of water acting as a siphon gave the necessary current of air. The air bubbles passed for about six hours and at all times the bubbles were regular and at a speed that they were barely countable as they passed through the alkaline solutions and standard acid solutions, respectively. The alkali and acid used in the titrations of the ammonia recovered were checked against each other several times, using methyl orange as an indicator. The same buret was used for both acid and alkali measurements and in all titrations involved.

Eight series of determinations gave the following results as tabulated. The standard acid used was 1.0695 0.2 *N* sulfuric acid and the alkali was 0.8405 0.2 *N* sodium hydroxide. The table explains itself.

[1] *J. Am. Chem. Soc.*, 33, 364.

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Series.	Grams NaOH per ½ liter.	Grams NaCl per ½ liter.	Hours standing.	Hours aëration.	Cc. H_2SO_4 soln. to collect NH_3.	Cc. NaOH soln. required for neutralization.	Cc. NaOH soln. required by theory.	
I–A	20	None	18	6	5.0	6.0	6.36	duplicates
A′	20	None	18	6	5.0	6.0	6.36	
B	20	40	17.5	6	5.0	6.0	6.36	duplicates
B′	20	40	17.5	6	5.0	6.0	6.36	
C	20	200	65	6	9.35	11.5	11.90	triplicates
C′	20	200	65	6	9.35	11.5	11.90	
C″	20	200	65	6	9.35	11.65	11.90	
II–A	20	None	17	5.5	9.35	11.70	11.90	
B	20	50	17	5.5	9.35	11.65	11.90	
C	20	150	17	5.5	9.35	11.65	11.90	
III–A	20	None	None	6.25	9.35	11.65	11.90	duplicates
A′	20	None	None	6.25	9.35	11.70	11.90	
B	20	45	None	6.25	9.35	11.65	11.90	
C	20	150	None	6.25	9.35	11.65	11.90	
IV–A	20	None	42	6	9.35	11.70	11.90	duplicates
A′	20	None	42	6	9.35	11.70	11.90	
B	20	45	42	6	9.35	11.60	11.90	
C	20	150	42	6	9.35	11.60	11.90	
V–A	10	None	None	6	9.35	11.70	11.90	duplicates
A′	10	None	None	6	9.35	11.70	11.90	
B	10	40[1]	None	6	9.35	11.60	11.90	
C	10	150[1]	None	6	9.35	11.60	11.90	
VI–A	10	None	22	5.75	9.35	11.70	11.90	duplicates
A′	10	None	22	5.75	9.35	11.80	11.90	
B	10	40[1]	22	5.75	9.35	11.90	11.90	
C	10	150[1]	22	5.75	10.28	13.0	13.09	
VII–A	10	None	None	6.5	9.35	11.75	11.90	duplicates
A′	10	None	None	6.5	9.35	11.75	11.90	
B	10	40[1]	None	6.5	9.35	11.75	11.90	
C	10	150	None	6.5	9.35	11.75	11.90	
VIII–A	10	None	42.5	6.5	9.35	11.70	11.90	duplicates
A′	10	None	42.5	6.5	9.35	11.70	11.90	
B	10	40[1]	42.5	6.5	9.35	11.70	11.90	
C	10	150[1]	42.5	6.5	9.35	11.65	11.90	

In the above work it is evident that there is a slight liberation of ammonia. The quantity is small but uniformly constant. With prolonged exposure to the caustic soda there is a slight increase in the amount of

[1] Part of the sodium chloride was placed in the beaker along with the dry uric acid, then covered with the dilute caustic soda solution. By this means some sodium chloride was present in the alkaline urate solution at all times, although the major portion of the sodium chloride had already been placed in the graduated flask before dilution to the mark.

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ammonia liberated. This amount seemed to be independent of the amount of sodium chloride present, for the same increase in acidity was obtained where no sodium chloride was present as where the solution was saturated with salt. The author is inclined to believe that the liberation of ammonia is not the main action of this particular decomposition of uric acid, since the quantity of ammonia evolved seems too small to justify any such conclusions.

In so far as the decomposition of uric acid under the influence of sodium hydroxide in the presence or absence of sodium chloride is concerned there seems but little room for objecting to the modified Steel-Folin method for determining ammonia in urine. In the results obtained above, one hundred cubic centimeters of the alkaline urate were used in every case. This volume was supposed to contain 0.05 gram of uric acid. In the actual determination as carried out with urine only one-fourth of this weight of uric acid is usually present, so the error introduced would be correspondingly less. The author feels that in the proposed modification of the Folin method there are compensating errors. In this laboratory it was found impossible to dissolve at room temperature as much as half the sodium chloride recommended by Steel. In this work it was found that 150 grams of sodium chloride would not completely dissolve in 500 cc. of 4 per cent. sodium hydroxide solution containing 0.25 gram of uric acid. By Steel's figures there should have been added to this volume of alkali solution 320 grams sodium chloride instead of the weight actually used. With the addition of the amount of sodium chloride recommended more than half remained undissolved. On passing air through this suspension, about one-third of the solution did not get thorough aëration because the undissolved sodium chloride settled to the bottom of the jar and refused to remain stirred up into the moving solution. With lack of stirring there would naturally be an incomplete removal of ammonia, even were it liberated. Since sodium hydroxide was used as the alkalinizing agent, perhaps more ammonia was liberated than should have been freed. With two oppositly directed errors present these may account for the closely concordant results of Steel.

The main interest in this paper has been in the quantity of ammonia that uric acid yielded from the action of dilute sodium hydroxide solutions. It seems that in so far as ammonia is given up by the uric acid, there is very little difference whether the sodium chloride is added or not. It may develop that constituents of urine other than uric acid are protected by the addition of sodium chloride in large amounts, but the author fails to see any justification for the use of the unduly large amounts of sodium chloride. At the present time, for the correction of the error due to the presence of ammonium magnesium phosphate, which seems

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to be present only in abnormal urines, according to Folin, it seems desirable to use sodium hydroxide rather than the sodium carbonate to free the ammonia. In general, it looks as though one is correcting an occasional appreciable error by introducing a frequent slightly smaller error.

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THE SYNTHESIS OF FATS BY THE ACTION OF ENZYMES.

By F. L. DUNLAP AND L. O. GILBERT.

Received September 1, 1911.

As a result of the various studies on the subject of lipolysis, it has been recognized that the reaction is never a complete one, the degree of hydrolysis depending on the conditions under which the experiments have been conducted. An hydrolysis of over 90 per cent. is not unusual, while on the other hand it may be considerably less, as for example, in the case of tributyrin when hydrolyzed by the lipase of the castor oil bean. Here Connstein, Hoyer and Wartenberg found but 9.5 per cent. hydrolysis after 24 hours.[1] In the latter case it is probable that no equilibrium is reached between the glyceride and the water and the products of hydrolysis, but rather that the acid produced either inhibits the lipolytic action when it reaches a certain concentration or the enzyme is destroyed.[2] The inhibition of fermentative processes by the normal products of such fermentation is well recognized, as in the case of lactic acid and alcoholic fermentation. That the lipolytic ferment, such as exists in the liver, pancreas, castor oil bean, etc., would not produce complete hydrolysis led to various successful attempts to synthesize fats through their action on mixtures of glycerol and the various fatty acids. Not only has the synthetic power of lipase been indicated, but of other enzymes as well.

With one exception experimental studies of synthesis due to lipase have been confined to this enzyme obtained from animal sources when acting on glycerol and the acids normal to fats. It is also worthy of note that many of these studies have been made with acids of exceptional occurrence in fats. This is seen, for example, in the work of Kastle and Loevenhart,[3] who studied pancreatic lipase and its synthetic effect on isobutyric acid and ethyl alcohol. Again, Hanriot[4] has produced monobutyrin by the action of glycerol on butyric acid by means of pancreatic

[1] *Ber.*, 35, 3988 (1902).

[2] Bradley [(*J. Biol. Chem.*, 8, 251 (1910)] is of the opinion that by increasing sufficiently the mass of the lipase, complete hydrolysis will ensue, but this is hardly in keeping with the views ordinarily expressed. For example, see Taylor [Univ. of California Publications, *Pathology*, 1, 35 (1904)].

[3] *Am. Chem. J.*, 24, 491 (1900).

[4] *Compt. rend.*, 132, 212 (1901).

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lipase, while Pottevin[1] has produced mono- and di-olein by use of the same ferment. Taylor[2] has prepared triolein by the action of pancreatic powder, glycerol and oleic acid. Bodenstein and Dietz[3] studied the synthetic effect of pancreatic lipase on butyric acid and isoamyl alcohol. Pottevin[4] has also studied the effect of the pancreatic ferment on oleic acid and various alcohols, as methyl, ethyl, propyl, isopropyl, etc., with the result that esterification was obtained. Twitchell's naphthalene-stearosulfonic acid which, as far as its properties are concerned, might be referred to as a synthetic enzyme, also has synthetic power, for in the absence of water it causes fatty acid and glycerol to condense.[5] Hamsik[6] has shown that a powder prepared from the mucous membrane of the small intestin of horses, sheep and hogs possesses synthetic power when applied to a mixture of oleic acid and glycerol. He has also shown that fat is synthesized through the action of the pancreatic lipase of the pig acting on palmitic and stearic acids and glycerol. The synthesis was identified by means of the decrease in the acid value.[7] A similar preparation from cattle and dogs possesses no such power.

Reference has been made to the one study recorded in the literature of the synthetic action of a vegetable lipase acting on glycerol and an acid normal to fat. As a result of this experimental work,[8] Taylor was able to synthesize triolein by means of the lipase of the castor oil bean. He mixed the glycerol with about one-fourth more than the molecular quantity of fatty acid necessary to produce the triglyceride. In all the tests the volume was 150 cc., to which was added 5 grams of the oil-free ricinus. After sealing, the flasks were shaken to emulsify. Controls were also used. After six months the flasks were opened and analyzed. The neutral fat produced was separated and the saponification number and iodine number determined. These were found to be, respectively, 185 and 81.2, sufficiently close to the theory to identify the product.

The work which we have to record was carried on several years ago and while its final results are similar to those obtained by Taylor, yet the method of proof is different and it has seemed worthy of permanent record. The work of Taylor was unknown to the authors at the time the experiments were conducted.

The enzyme used for this work was that found in the castor oil bean. It was deemed unnecessary to work with the very active cytoplasm as

[1] *Compt. rend.*, 136, 767 (1903).
[2] *J. Biol. Chem.*, 2, 102 (1906).
[3] *Z. Elektrochem.*, 12, 605 (1906). Dietz, *Z. physiol. Chem.*, 52, 279 (1907).
[4] *Ann. de l'Inst. Pasteur*, 20, 901 (1906).
[5] THIS JOURNAL, 29, 566 (1907).
[6] *Z. physiol. Chem.*, 59, 1 (1909).
[7] *Ibid.*, 71, 238 (1911).
[8] [Univ. of California Publications, *Pathology*, 1, 33 (1904).]

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described by Nicloux,[1] but the bean was, after decorticating, thoroughly ground and exhausted with ether and used in this form. Many experiments were conducted in order to find a suitable emulsifying agent, the one proving most satisfactory being flaxseed. When glycerol, oleic acid, flaxseed, and the oil-free castor bean are thoroughly ground together an emulsion is formed which will persist for days. It has been shown by one of us that the ungerminated flaxseed was devoid of lipolytic power,[2] which is amply shown by the blank test hereafter to be described. If this flaxseed possessed lipolytic power it would without question, in view of our present knowledge of the subject, also possess a certain degree of synthetic power. The blank experiment amply shows that it was not synthetic in the least.

In other experiments which have been published by one of us[3] it was found necessary to use preservative agents, such as chloral. In the present series of experiments, such agents were unnecessary as is shown in the blank experiments. Molds and bacteria do not thrive in the absence of water, or when water is present only in small amounts.

The method used was briefly as follows: Glycerol, oleic acid, flaxseed, and the oil-free castor oil bean, in a finely comminuted form, were thoroughly triturated in a mortar until an emulsion was formed, which was divided among several weighed flasks. An estimation of the acid was made at once in the contents of one of the flasks, the other flasks being reserved for the estimation of the acid value on succeeding days. The blank experiment was made in exactly the same way, except that the amount of oil-free castor bean was replaced by flaxseed. Considerable work was done before a method was found for getting concordant results in the estimation of the oleic acid in this emulsion. The method which proved satisfactory consisted in the treatment of the emulsion in the flask with ether, breaking up the emulsion thoroughly by means of a glass rod flattened at the bottom, and subsequent titration by means of a standardized alconolic potash. It will be seen from the following figures that the amount of oleic acid in the blank remained practically constant, whereas in the case of the two experiments where the castor oil bean was used, there was a marked and steady decrease in the amount of oleic acid. This decrease could only have been due to the esterification of the oleic acid. The fact that the castor bean enzyme has synthetic power is shown very clearly by these results and it did not seem necessary to attempt an isolation of the product in order to prove this point. These results do not show whether the combination of the oleic acid and the glycerol produce a mono- or di-glyceride before the triglyceride is

[1] *Compt. rend.*, 138, 1112, 1288, 1352 (1904); 139, 143 (1904).
[2] Dunlap and Seymour, THIS JOURNAL, 27, 935 (1905).
[3] *Ibid.*, 27, 940 (1905).

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produced, but judging from the results obtained by Pottevin and Hanriot, whose work has been discussed, it is possible that the interaction between the glycerol and the oleic acid takes place in three stages. It is, however, worthy of note that Taylor isolated only triolein.

In the experimental data which follow, the material for preparing the emulsion was weighed on a rough balance and in each of the three studies recorded the following substances were used:

5 grams oil-free castor bean.
5 grams flaxseed.
25.5 grams glycerol.
16.7 grams Kahlbaum's oleic acid.

In the case of the blank, over 10 grams of flaxseed were used and no castor oil bean. The glycerol was used quite largely in excess of the amount theoretically necessary to esterify the oleic acid.

Blank experiment.

Time.	Milligrams oleic acid in 1 gram of the mixture.
At once	315.5
After 2 days	319.0
After 4 days	315.7
After 6 days	314.8
After 8 days	315.5
After 11 days	314.9

Experiment using castor oil bean.

Time.	Milligrams oleic acid in 1 gram of the mixture.
At once	337.3
After 2 days	322.0
After 3 days	320.2
After 6 days	311.6
After 9 days	290.5
After 11 days	248.6

This shows a combination of 88.7 milligrams of oleic acid with glycerol, that is, a disappearance of over 26 per cent. of the total oleic acid present.

Another experiment, however, which did not run so long as the one recorded above, gave the following data:

Time.	Milligrams oleic acid in 1 gram of the mixture.
At once	302.7
After 2 days	287.2
After 4 days	257.6
After 7 days	230.8

There seems little doubt but that the decrease in the free acid would have been greater had the experiment been carried on for a longer period. Unfortunately it was impossible to extend this work at that time. The

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results here reported, as well as those obtained by Taylor, show undoubtedly that the enzyme of ricinus has synthetic power.

Since this article was written there has appeared in the *Z. angew. Chem.*, 24, 385 (1911) an article by Adolf Welter. He discusses some experimental work on the reversibility of enzyme action and gives some results of the synthesis of fats from fat acids and glycerol through the action of the castor oil bean ferment. Welter uses blanks identical with mixtures used, only heated to 60–80° to destroy the activity of the lipase. He recognizes the change brought about by the decrease in acid values.

The experimental work on this subject was performed at the University of Michigan.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, HYGIENIC LABORATORY, U. S. HEALTH AND MARINE HOSPITAL SERVICE.]

THE STABILITY OF THE PHOTOGENIC MATERIAL OF THE LAMPYRIDAE AND ITS PROBABLE CHEMICAL NATURE.[1]

BY F. ALEX MCDERMOTT.

Received August 16, 1911.

One of the oldest and at the same time one of the most important observations relative to the chemical processes involved in the production of light by living creatures, is that the photogenic tissues may be dried, preferably in the absence of air (oxygen), and preserved, again out of contact with air (oxygen), for considerable periods, without losing the power to evolve light when moistened in the presence of air (oxygen). This fact, which seems so remarkable at first sight, appears to have been discovered by Reaumur in his work on the luminous bivalve *Pholas dactylus*, in 1733. The observation was repeated by Spallanzani in 1794 and 1796, by Carradori in 1798, by Carus in 1864, and by Dubois in 1886. Spallanzani extended it to the luminous *Medusae*, Carus to the fireflies (*Lampyridae*), and Dubois to the *Myriapoda* and the *Elateridae*. Pflüger, in 1875, seems to have regarded the luminous tissue of the *Lampyridae* as of too little vitality to exhibit this phenomenon, but the recent work of Kastle and McDermott on this same subject indicates that his conclusion was probably based on material dried in the air.

Kastle and McDermott showed that if the luminous organs of the common firefly of this region, *Photinus pyralis*, were dried *in vacuo* with a residual atmosphere of hydrogen, and subsequently sealed *in vacuo* or in hydrogen, the tissue will retain its photogenic power, and exhibit

[1] Presented at the 44th Annual meeting of the American Chemical Society, Section on Biological Chemistry, Indianapolis, Ind., June 28, 1911.

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it when moistened, for thirteen months after preparation. Since the latter paper was written, material prepared at the same time as that referred to above has been found to be active almost eighteen months after preparation, and so far as could be judged, without appreciable depreciation. The material preserved *in vacuo* seemed to be slightly more active than that preserved in hydrogen. Kastle and McDermott also showed that the photogenic material was not always entirely exhausted when the dried tissues were first moistened, but that if carefully dried again, the production of light might be repeated two or even three times with the same specimen. The present author has also shown that if the dried photogenic tissue be moistened with a three per cent. solution of hydrogen peroxide, a brighter light is produced than if water alone is used, and the hydrogen peroxide is decomposed.

It has been our experience that if the tubes in which the dry luminous tissue was sealed were broken and the tissue exposed to the air, it rapidly lost its photogenic power, and it had been observed that dried organs of lampyrids thus exposed to the air on damp days glowed feebly for a long time, apparently exhausting their luminous activity. Consequently considerable disappointment was experienced when it was found that a tube in which some 500 of these photogenic organs had been sealed in hydrogen had been accidentally broken; a few of the organs were tested and found to have apparently entirely lost their photogenic activity. An ordinary rubber stopper was placed in the tube, and the latter laid away for possible future use. On three occasions since the breaking of the tube, this stopper has been removed to secure a few of the dried organs for various experiments, without any attention being paid to possible residual photogenicity; but when the tube was opened a fourth time, and a few organs removed on April 29, 1911, about 6 months after the tube was broken, it was thought worth while to test them in the matter of light emission. Accordingly about a dozen of the dried organs were placed in a mortar, ground to a powder, and a few drops of water run in upon them. A faint but distinct yellowish glow resulted, showing that in spite of six months' exposure to air, without especial precautions and at room temperature, a certain amount of the photogenic substance still remained unoxidized. At a still more recent date, May 16, 1911, another lot of these dried organs was removed from this same tube and ground with 3 per cent. hydrogen peroxide; a much brighter light resulted than that produced by water alone and the hydrogen peroxide was actively decomposed. The light produced appeared somewhat reddish in tone.

Through the kindness of Dr. W. W. Coblentz, of the Bureau of Standards, the author was enabled to test the effect of the temperature of liquid air upon the fresh luminous tissue, and upon the same lot of dry material

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as referred to above. So far as the power to produce light is concerned, this temperature has no effect upon the luminous tissue, fresh or dry. A living lampyrid (*Photuris pennsylvanica*) dropped into a test-tube immersed in liquid air flashed rapidly for a few seconds, but was soon overcome by the cold, and fell back in the tube, frozen stiff; meanwhile, the luminous organ began to shine brilliantly, but the brilliancy rapidly diminished, the diminution in brilliancy being accompanied by a change in the color of the light, which become very reddish. The light finally disappeared entirely, or very nearly so. On warming to the room temperature, the light first appeared reddish, and with increase in intensity become more and more like the normal light of the insect. The insect was dead, but the luminous tissue continued to glow for some time. The effect on a freshly detached luminous organ was the same, except that the vapors from the liquid air acted as a powerful stimulus to the tissue when first placed upon it. Grinding the tissue in liquid air did not destroy, or apparently in the least weaken its power to emit light on restoration to normal temperature. With the dried tissue from the 1910 lot, previous immersion in liquid air, or grinding while immersed in the liquid, had absolutely no effect, since when moistened with hydrogen peroxide solution after such treatment, the tissue glowed as strongly as before. Experiments have also been performed with liquid sulfur dioxide and liquid ammonia, on the dried tissue. Both of these liquefied gases permanently destroy the photogenic power of the dried tissue, the latter changing the color of the organs to a deep salmon. Sulfur dioxide has been known for some time to destroy the photogenicity of the fresh tissue, and of the dried tissue after moistening; ammonia in solution in water, however, has apparently acted as a stimulus to the activity of the fresh tissues.

Another previous observation of the author is of interest here: A number of luminous organs from *Photinus pyralis* had been ground to an emulsion with glycerol immediately after removal from the insects. A faint glow persisted for some moments after the emulsion had been poured into a bottle, but the next morning no luminosity was visible, nor was any excited by agitation, and it was concluded that the photogenic material had spent its powers. The bottle was subsequently forgotten, and not noticed again for about six months, when it was washed up for other use. As the glycerol emulsion was poured out into running water, several bright points were noticed, and upon darkening the room and washing the bottle out with cold water, quite a display of these points of light was observed, some of the larger fragments glowing for two or three minutes before extinction. Glycerol has usually been regarded as an unsuitable medium for the preservation of photogenic organs, and has even been regarded as poisonous to the ligh-producing power, but

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it would seem from the foregoing notes that such organs may retain a portion of their photogenic power for at least six months in this medium. Histologic fixing fluids without exception appear to permanently destroy the photogenic power of the tissue; many of these fluids are powerfully oxidizing in nature.

With regard to the stability of the material in the numerous other photogenic forms, but little can be said. *Pholas* has been said to preserve its photogenic power, when preserved in honey, for a year, needing only the application of warmth to call forth an exhibition of the light. A few experiments have been made with the photogenic bacteria, from which it seems probable that if a culture of these organisms could be taken to complete dryness when at their maximum activity, the dried culture might show luminescence when moistened; the experiments, however, were not sufficiently satisfactory to warrant definit conclusions on this point. Macfadyen has found that if photogenic bacteria are cooled to the temperature of liquid air, and then allowed to return to their normal temperature for growth, they grow and luminesce again with practically unabated vigor. But if while at the temperature of liquid air, the luminous microörganisms are ground in a mortar, they fail to exhibit luminosity or growth when the temperature returns to normal.

All of these facts show parallelism to other well-known facts in biological chemistry, *e. g.*, the drying of ferments to retain their activity. Still another point of similar interest brought out by Kastle and McDermott was that the dry photogenic tissue could be heated to 100° without perceptibly injuring its activity upon moistening.

It must be, therefore, that atmospheric oxygen has less effect upon the photogenic material of these forms, especially when dry, than has ordinarily been supposed, and therefore the isolation of this material in its non-oxidized condition while difficult may not be a problem hopeless of solution.

Much work has been done, and much of it is conflicting, upon the question of whether or not the photogenic process is an oxidation. The balance of the evidence now is strongly in favor of the oxidation theory in the majority of cases—so strongly, in fact, as to leave but little room for doubt. The photogenic bacteria glow more brightly in oxygen, and are extinguished, though not killed, in neutral gases. The photogenic organs of the *Lampyridae and Elateridae* involve a network of anastomosing tracheal capillaries connecting directly with the breathing spiracles. The luminous organs of fish and cephalopods have a similar network of capillaries connected with the circulatory system. The dried photogenic material of the *Lampyridae* glows most strongly when moistened in oxygen and certain oxidizing gases, and but faintly or not at all in

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neutral gases; it glows more brightly when moistened with a solution of a powerful oxidizing agent (hydrogen peroxide) than when water alone is used. Certain *per se* non-luminous myriapods and worms emit secretions which become actively luminous when ejected into the air or water. These are a few of the points tending to show the oxidative nature of the photogenic process.

Dubois' view that the light production in *Pholas* and in the *Elateridae* is due to a reaction between two substances, extractable from the photogenic tissues by different processes, is of considerable interest. Especially significant is his observation that one of his extracts may be replaced by chemical substances, such as potassium permanganate, lead peroxide and barium peroxide, and from this it seems not improbable that his oxidizing liquid extract may be a solution of an organic peroxide, possibly of a specific nature, especially since he failed to secure the production of light when he substituted laccase for the oxidizing extract.

The isolation of the photogenic compound is a baffling problem, as we know little or nothing as to its nature, but a few speculations as to its probable nature may not be amiss. The view that the "phosphorescence" was due to the element phosphorus was probably the first view advanced which would seem in any degree reasonable by modern chemical standards, and this view has had its supporters up to quite recent times. It needs very little consideration to see that it is impossible, however, and the chemical fact that there is no free phosphorus in the tissues practically settles it. A more rational view was that of Lavoisier, that the light was produced through the spontaneous combustion of phosphine, produced by the decomposition of protoplasm; this view has also had its supporters up to modern times. Again this theory fails for the want of isolation of any phosphorus compounds resembling phosphine from the luminous tissues. Watase's view that the luminosity was connected with the contractility of protoplasm does not satisfy the chemical requirements of the case.

From the standpoint of biological chemistry, the first rational view was probably that the photogenic compound was a fat. Certain fats were known to exhibit faint luminosity when undergoing slow oxidation. Many fats blacken with osmic acid, and it was found that the photogenic tissues of the *Lampyridae* stained readily with this compound. Thus there seemed to be some evidence of the fatty nature of the compound. Macaire, however, advanced the theory that the compound was albuminous, as it was coagulated by heat, and in this he was followed by Kölliker. Heinemann found phosphoric acid in the ash of the luminous organs of the cucuyo though earlier investigators obtained conflicting results on this point. Phipson regarded the photogenic material as nitrogenous, and stated that on decomposition it gave off an odor of propylamine.

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Another point of view stands us in good stead here. In the majority of cases, the luminous tissues of animals appear to be developed embryologically from the fatty layers of the body (see Dahlgren and Kepner). In some cases, of course, this does not hold, as in the shark *Spinax niger* whose luminous organ is developed from squamous epithelium; but in many, if not in most cases of the higher luminous forms, the derivation from the fat tissue is the usual embryologic source of the photogenic organs. This fact, taken with what has been brought out previously, points to the supposition, for it can be little else, that in the *Lampyridae* and many other photogenic forms the photogenicity is the result of the oxidation of a lipoid (phosphatide) containing an unsaturated aliphatic radical, and probably an albuminous grouping. It is interesting to note that Radziszewski includes protagon (lecithin) among the organic compounds possessing phosphorescence.

Some attempts to isolate a photogenic material by extraction of the fresh organs with ether, alcohol or chloroform, in an atmosphere of hydrogen, all failed; however, it is hoped to extend this method of investigation to other solvents, especially to water containing no dissolved oxygen.

With the bacteria it seems unlikely that this view will hold good, and the same may also be true of the *Noctilucae*, *Pyrocystae*, etc. The photogenic bacteria can produce light in a medium as simple as water containing one per cent. of asparagine and three per cent. of sodium chloride, so that it would seem that here the product of metabolism oxidizable with photogenicity might not be so very complex.

Another suggestion is worthy of consideration so far as the possible differences between the photogenic material in different luminous forms: It might possibly be that there would be found to be organic "Photophore" groupings, just as we now have fluorophore and chromophore groupings. That this is indeed probable is indicated by the work of Delépine and of Trautz. The latter showed that the spectrum of the light emitted when pyrogallol is oxidized by perhydrol in the presence of formaldehyde covers very nearly the same spectral area as that of the emitted light of the firefly, and that light produced in a good many cases of chemiluminescence is greenish,[1] *i. e.*, like the firefly's light, has its point of maximum intensity near the yellow-green, the part of the spectrum having the maximum radiant efficiency. It may be then that the "Noctilucin" of Phipson, the "Luciferin" of Dubois and the "Photogen" of Molisch are different chemical conpounds having similar or related photogenic groupings in the organic radical.

[1] Poliman.i has recently asserted that the luminosity of *Pyrosoma* cannot be due to oxidation, and cites its greenish color as a basis for this view—a statement which does not seem to be well founded, in view of the large number of known chemiluminescent oxidations which produce a greenish light.

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In summary: The photogenic compound present in the *Lampyridae* is much more stable towards atmospheric oxygen than has usually been thought, especially when dried out of contact with the air; it presents points of similarity to other known biological products; from embryological and chemical considerations it appears probable that it is an albuminous lipoid (phosphatide).

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WASHINGTON, D. C.

NEW BOOKS.

Messungen elektromotorischer Kräfte galvanischer Ketten with wässerigen Elektrolyten. By R. ABEGG, FR. AUERBACH AND R. LUTHER. Wilhelm Knapp, Halle, 1911.

The purpose of this exceedingly valuable number of the series (No. 5, "Abhandlungen deutschen Bunsen-Gesellschaft") is to summarize all the observed electromotive forces of reversible systems in order that they may be available for the consideration of the general problem of affinity. The work is divided into three parts: the first containing a chronological list of all the systems which have been studied; the second a systematic selection of the most reliable results, grouped together under the elements considered; while the third is devoted to the consideration of single or normal potentials.

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The great value of this work for the purpose of reference will be apparent from the above; even a glance through it shows that it should be found on the desk of every investigator. J. L. R. MORGAN.

Handbuch der Mineralchemie. By C. DOELTER, with the aid of more than fifty associates. In four volumes, 50–60 parts (bogen). First part of Vol. I, 160 pp. Price, M. 6.50. Th. Steinkopff. Dresden. 1911.

The introduction of this new work by Prof. Doelter is short and to the point, and in it the general problems of the subject are, for the most part, well stated. The work is of the widest scope, aiming to give in a more complete way than any other extant the data in this department of chemistry. Besides matter on mineral synthesis, the genesis of minerals, etc., articles are promised on silicate melts, cement silicates, glasses, slags, artificial gems, and the manufacturing processes for technically important minerals.

No strikingly original element, either of classification or method of treatment, appears; it may therefore be expected that the chief value of the book will be as a compilation of data and as an index to literature. In these respects the first instalment seems to be very complete, though only time and use can determin their accuracy.

To judge from these first printed pages, the most general criticism to be passed on the work is that it does not lay sufficient stress on the quantitative side of the subject. No quantitative data at all are given on the optical characteristics of the important carbonates of calcium, magnesium and iron, necessary as these are to the analysis of mixtures, and important as physical constants. The characterization of vaterite, about which much is said, is not based on sufficient quantitative data (p. 114) to satisfy the reader that it is really a distinct form of calcium carbonate. No doubt geological speculation regarding the genesis of minerals has a rightful place in a work of this kind when its foundation is not too meager; it is germane to the subject, is often suggestive to the investigator, and will save much reference-hunting; but it seems to the writer that it forms too large an element here. It is hardly pardonable in a scientific text-book to include so much under the heading "it is possible" (p. 133).

The qualitative viewpoint crops out strongly in this statement of Doelter (p. 8): "In no case, however, is it admissible to designate an artificially prepared anorthite, diopside, ruby, simply as anorthite, etc., since these names belong exclusively to the natural products." We must take care here not to confuse the essential properties of a mineral and its genesis in nature. Anorthite and diopside have been prepared in the laboratory which possess all the essential properties of each. This can be settled and has been settled by quantitative measurements of these properties. True, the minerals of nature are rarely pure, and it

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is obviously the pure "end members" of the solid solutions in nature which have the first claim to a determination of their constants; constants of the others are valueless unless the composition is also known. Doelter's statement that a synthetic mineral, in order to deserve the name "mineral" "must possess all the properties of the natural product, essential as well as secondary," must be interpreted in the light of the above. Natural specimens of the same mineral vary as much from one another as they do from the pure synthetic product, and it is also certain that the same mineral in nature is often formed in a number of different ways.

The statement (p. 8) that the artificial sapphire is isotropic is incorrect; many, if not all, the artificial rubies and sapphires now on the market are single uniaxial crystals.

This first instalment of Mineralchemie treats of the forms of carbon; Diamond by Doelter, Graphite by Amberg, and Schungite by Heinisch; the Carbonates of Calcium, Magnesium, and Iron, by Linck, a beginning of the Carbonates of Sodium by Wegscheider, and Analytical Methods by Dittrich and by Kaiser. E. T. ALLEN.

Die Kristallgruppen. By DR. E. SOMMERFELDT. Dresden. Theo. Steinkopff. 1911. pp. 79, Fig. 64. Price, 3 M.

The author describes a series of models with which may be illustrated the essential features of crystal structure, in a manner more easy of comprehension than is possible with models constructed on the principle of the Sohncke point system. The new models of the simpler structures are made of needles on which balls are strung at definit intervals. These needles are struck into supports in such a way as to cause the balls to be spaced in accordance with the fourteen Bravais types of structure (Raumgitter). Stereoscopic photographs of these arrangements, with the simple crystal forms corresponding to them, are printed in the proper positions for viewing through an ordinary stereoscope. The illustration of hemihedral and other partial forms is accomplished by replacing the balls with little bars arranged along the needles with their long axes in parallel directions or in directions that have spiral relations with one another, like the arrangement of leaves on a stem. W. S. BAYLEY.

Journal of the Washington Academy of Sciences. Published semi-monthly except July, August and September, when monthly. Subscription price, to members for annual dues, to members of affiliated societies, $2.50; to others, $6.00. Does not exchange with other publications.

A journal for the publication of short papers in any science. It may serve a useful purpose as a medium for scientific news in this large colony of scientists, and in acquainting the scientific men of Washington with the work of their fellows in other lines; also in some cases in affording an

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opportunity for the publication of certain articles which would otherwise have to wait over long. However, it is much to be hoped that this new journal will not prove a temptation for the unnecessary multiplication of papers or a vehicle for half-done ideas with which the pages of science are already overburdened.

E. T. ALLEN.

Neuere Erfolge und Probleme der Chemie. VON EMIL FISCHER. Julius Springer, Berlin. 1911. pp. 30.

No essay from the pen of the great master of organic chemistry could fail to attract attention, and every one concerned with the progress of civilization will find interest in this brief paper. Here is recorded the report of an experimental lecture, delivered in the presence of the Emperor on the occasion of the foundation of the two great Kaiser Wilhelm chemical research laboratories. It will be remembered that the endowment of these institutes was the chief feature of the hundredth anniversary of the founding of the University of Berlin. In the lecture, the remarkable progress of chemistry during the last few decades is sketched in vivid words. The chemistry of high and low temperatures, radioactivity and organic synthesis (especially of products of value to medicin and commerce) are all touched upon, as well as other striking aspects of the rapidly developing science.

The founding of these laboratories under such favorable auspices gives yet another impulse to the study of chemistry in Germany; and one cannot but hope that other nations, especially our own, will follow Germany's good example.

T. W. RICHARDS.

National Notebook Sheets for Laboratory Work in Chemistry. By ARTHUR S. DEWING. L. E. Knott Company, Boston. 8.5 × 10 ins. single sheets, $1; complete book, $1.64.

This is a laboratory manual arranged on the loose leaf plan; the directions for performing each of the eighty or so experiments are on single sheets. Many experiments are supplemented by exercises which consist of questions bearing upon the preceding experiments and of topics for written exercises and compositions. Descriptive matter under the caption of "Notes" is inserted at frequent intervals. The experiments and descriptive text cover about fifteen topics, including, besides those usually found in high school books, thermochemistry and electrochemistry. The illustrations are numerous and as a rule quite helpful, though occasionally superfluous; for example, the ordinary test-tube rack with four test-tubes appears no less than twenty times. If any criticism were to be offered of the book as a whole it would be the inclusion of experiments on Faraday's Law, Chemical Equilibrium, and Mass Action.

There are but few errors in the book; one important one should be noted. The author in Notes A 20 and A 40 has fallen into the difficulty

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of trying to make the older definitions of acids, bases and salts coincide with the newer definitions; doubtless this error will be corrected in subsequent editions.

On the whole the author's purpose, namely, to prepare experiments, exercises, and descriptive matter in a flexible manner for high school pupils, has been well accomplished. L. C. N.

Qualitative Chemical Analysis. By W. W. SCOTT. New York, D. Van Nostrand Company. 14 x 22 cm., pp. 165. Cloth. Price, $1.50.

"The purpose of this manual is to furnish a practical, modern guide for students studying Qualitative Analysis." The modern character refers to the brief statements of the electrolytic theory of solutions, of reversible reactions, the law of mass action, solubility product, and amphoteric electrolytes. In attempting the utilization of the ionic theory many of the expressions are loose and peculiar: "depends on the degree of dissociation of the H• and the acid radical." The terms used presuppose considerable familiarity with the general conceptions of Physcal chemistry or the expenditure of a large portion of the class-room time in order to make the student familiar with these ideas. The methods employed are well chosen and generally the descriptions of the processes are clear and the arrangement comparatively easy to follow. There is a tendency, however, to crowd the schemes, which detracts from the workmanship of the book; otherwise it presents a good appearance. There are not many typographical errors: on page 116 W. M. Noyes should read A. A. Noyes, p. 95 ni• should be Ni•, etc. One of the main features of this work is the introduction of general descriptive chemistry, which occupies nearly one-sixth of the text. The properties and occurrence of the elements and their compounds are listed and in many cases rare and uncommon occurrences are given. It is a question whether it is advizable to incorporate so much of this descriptive matter in a text on qualitative analysis, as the student is already provided with this in his general text on chemistry. Another feature is the introduction at the beginning of the discussion and separation of each group of a list of reagents to be used. There is also a list of all reagents used with their strength expressed in normal and gram or per cent. concentration given in the Appendix. Many of the reagents are thus listed many times, which is an unnecessary duplication and the particular reagent is also stated in the description of the process. The scheme for the analysis of metals and alloys is not all that is desired. The abbreviations A. w. for atomic weight and S. g. for specific gravity are not the ones usually employed. A. T. LINCOLN.

Die Bestimmungsmethoden des Wismuts und seine Trennung von den anderen Elementen. VON PRIVÄTDOZENT DR. L. MOSER. (*Die chemische Analyse. Sammlung*

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von Einzeldarstellungen auf dem Gebiete der chemischen, technisch-chemischen und physikalisch-chemischen Analyse. Band X.) 16 x 25 cm., pp. 126. Stuttgart: Ferdinand Enke, 1909. Price, paper, 4 marks.

The historical account is followed by a description of the occurrences of bismuth and then there is given the methods for obtaining metallic bismuth and an enumeration of its properties and uses. The main portion of the book is devoted to the qualitative and quantitative methods for its detection, separation and estimation. Under the qualitative methods are given the qualitative reactions, microscopic tests, dry tests, and methods for separation from other elements. The quantitative methods are described under the following headings: 1. Gravimetric, wherein bismuth is determined as the oxide, metal, oxychloride, phosphate, sulfide, molybdate, sulfate, arsenate and chromate. 2. Volumetric, which includes the chromate, iodate, arsenate, oxalate, hypochlorite, sulfide, molybdate and phosphate methods. 3. Colorimetric. 4. Gasometric. 5. Electroanalysis. 6. Methods for the separation of bismuth from the other metals—this comprizes about one-fifth of the text. 7. Special methods are listed for the analysis of special compounds containing bismuth, such as alloys as well as organic and pharmaceutical preparations. The author considers the phosphate method the best and it can be used either gravimetrically or volumetrically, while the electrolytic methods, amalgam of Vortman and the wire gauze cathode of Brunck and the rapid methods of Fischer and of Sand are recommended. The work comprizes a comprehensive exposition of the methods which are well arranged with ample detail for use, and with references to the original literature.

A. T. LINCOLN.

A Systematic Handbook of Volumetric Analysis. By FRANCIS SUTTON. 10th edition by W. L. SUTTON and A. E. JOHNSON. Philadelphia: P. Blakiston's Son & Co. pp. xiv + 621. Price, $5.50.

Of this standard work we are informed that nine editions, 15,750 copies in all, have been sold. The junior authors tell us in their editor's preface that the references are now printed at the bottom of the page, that the sections on the pipet, measuring flask and weights and measures have been rewritten, the data having been supplied by R. J. Glazebrook, of the National Physical Laboratory. The term normal solution has been defined more clearly as follows: "A normal solution of a reagent is one that contains in a liter that proportion of its molecular weight in grams which corresponds to one gram of available hydrogen or its equivalent." The most recent procedure for the technically complete analysis of ammoniacal liquors has been supplied by W. F. Carpenter. The section on ferrocyanides has been improved. Knecht's process for iron with titanous chloride is described. The determination of sulfur in iron and steel as carried out at the National Physical Laboratory is included. Under

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magnesium, manganese, mercury, nickel, dissolved oxygen, sugars, titanium, vanadium, zinc, acetone, oils, fats and waxes, phenols, cresols, urea, water and sewage, new matter has been inserted.

EDWARD HART.

RECENT PUBLICATIONS.

ABDERHALDEN, E.: **Handbuch der biochemischen Arbeitsmethoden.** 5 Bd. Wien: Urban & Schwarzenberg. 31 M.

ABDERHALDEN, E.: **Die Bedeutung der Verdauung für den Zellstoffwechsel im Lichte neuer Forschungen auf dem Gebiete der physiologischen Chemie.** Wien: Urban & Schwarzenberg. 39 pp., 1 M.

ABEL, R.: **Bakteriologisches Taschenbuch.** 15 Aufl. Wurzburg: A. Stuber. 8°, 137 pp., 2 M.

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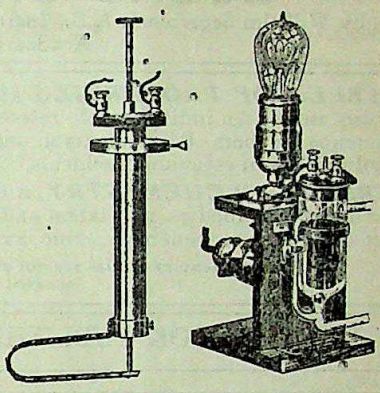

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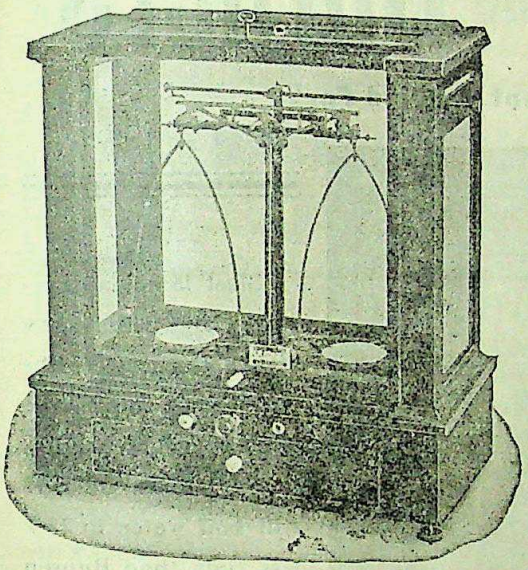

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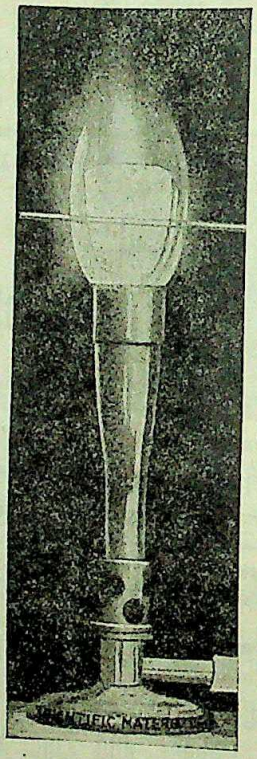

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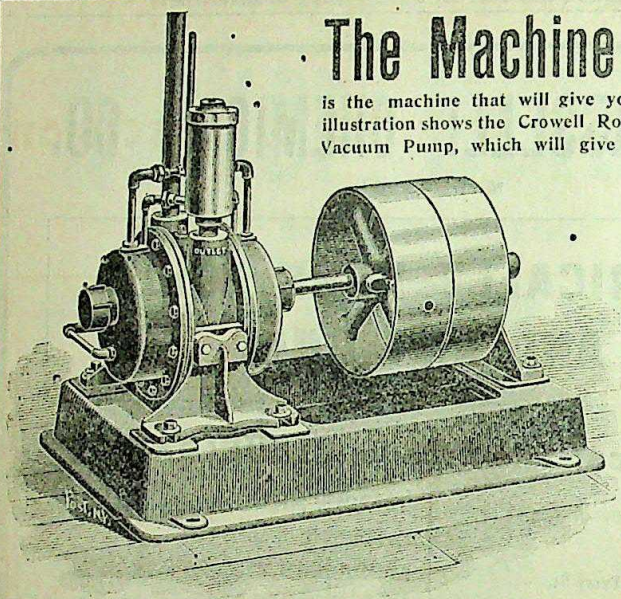

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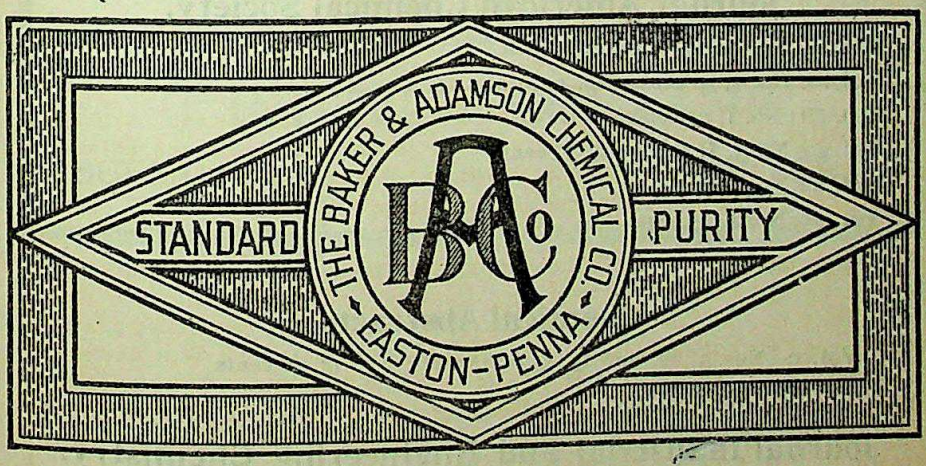

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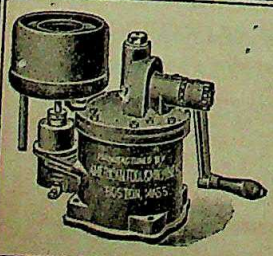

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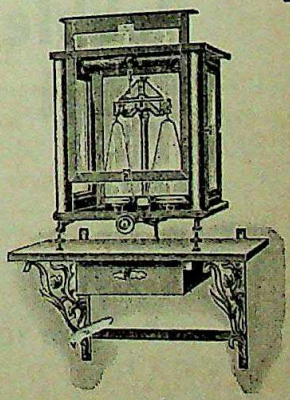

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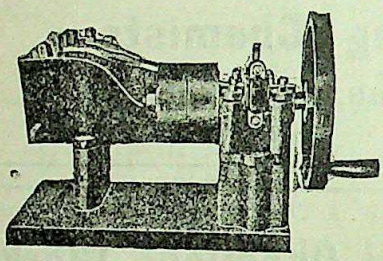

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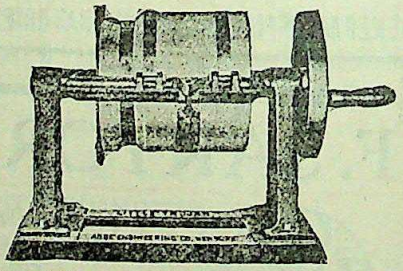

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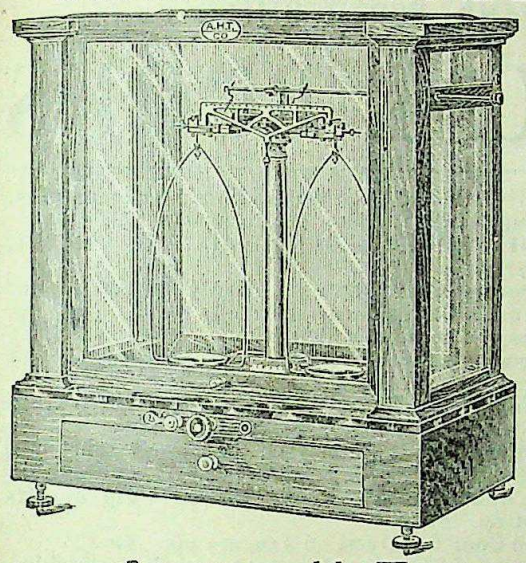

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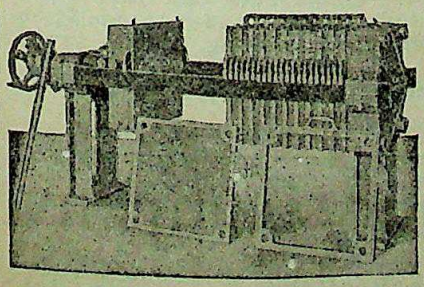

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Issued with the December Number, 1911.

Proceedings.

COUNCIL.

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Wooldridge, P. J., Kentucky Title Bldg., Louisville, Ky.
Wright, Philip A., 1012 Walnut St., Columbia, Mo.
Zia, Z. Zungtsoo, 803 Hartley Hall, Columbia University, New York City.

President Smith has appointed Dr. Wm. J. Schieffelin representative of the American Chemical Society to the Local Committee of the International Congress for the Prevention of Accidents and Industrial Hygiene to meet in Milan in 1912.

BOARD OF DIRECTORS.

The Directors met at the Chemists' Club, New York City, on Tuesday, October 24th, at 8 P.M., President Smith in the chair and all members present.

The question of advertizing in the Society's journals was considered and it was voted that President Smith and E. G. Love be constituted a special committee of the Directors with power to arrange with Mr. Mack for the termination of his contract as advertizing agent, and in the event of a satisfactory adjustment of the matter, to proceed at once to negotiate a contract with Mr. E. J. Gibling on the basis of his letter of October 23d.

It was further voted that on the report of this committee being received, the officers of the Society be authorized and directed to close the contract approved by them.

It was voted that one hundred and fifty dollars be granted toward the publication of the Annual International Tables of Physical and Chemical Constants for the year 1910, it having been stated to the Directors that the members of the Society on such grant being made would be entitled to a discount of twenty per cent. from regular prices on the published volume.

It was voted that President Smith and T. J. Parker be appointed a committee to consider changes of the Constitution which seem to be necessary from legal opinions transmitted to these gentlemen, in order that recommendations might be made from the Directors to the Council at the time of the winter meeting.

It was voted to add $404 to the budget for Chemical Abstracts for the year 1911.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary*.

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MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

SOUTHERN CALIFORNIA SECTION.

On Saturday morning, Sept. 9th, members of the Section visited the beet sugar factory of the Holly Sugar Co. After an inspection of the plant the party was taken to Huntington Beach Hotel, where, as guests of the Sugar Company, they enjoyed luncheon and surf-bathing.

The October meeting was held on the 19th at the University Club, Los Angeles, preceded by a dinner at 6 o'clock. Mr. Edgar S. Baruch presented a paper on "The Manufacture of Beet Sugar."

B. A. OLSHAUSEN, *Secretary.*

PUGET SOUND SECTION.

The September meeting was held on the evening of the 20th in honor of Dr. F. G. Cottrell, of the Bureau of Mines, who spoke of the work of the Bureau, also of his work on the settling of smelter fumes.

The October meeting was held at the Faculty Club House at the University of Washington on the evening of the 18th, with Dr. Hugo Schweitzer, of the N. Y. Section, present, who spoke on Ehrlich's Chemotherapy; also on the synthetical manufacture of various compounds.

J. H. LINTON, *Secretary.*

CONNECTICUT VALLEY SECTION.

The first meeting of the season on October 7th was called to order in the chemical lecture room, Trinity College, at 8.15 P.M., by Chairman Farrell. Considerable routine business was transacted, and nine new names were proposed for associate membership, after which two very interesting and instructive papers were presented as follows: "Some Ammoniacates of Ammonium Sulfocyanide," by Professor Bradley, and "The Sherardizing Process," by Mr. Rowland.

The fourth meeting of the Section was held in a parlor of the Hotel Garde, Hartford, Conn., November 4th at 8 P.M. Mr. Sternberg having obtained a room for the Section in the Hotel Garde free of charge, it was voted that in the future all the meetings should be held at this Hotel except where laboratory equipment was needed, in which case meetings are to be held at Trinity College. Several associate members were announced as having become me[illegible]rs of the Section through the action of the Executive Committee. [illegible] Society then listened to two papers: "The Action of Trimethylamine on Alkyl Halides," by Professor R. Rex Renshaw, and "Economic Sea-weeds," by Mr. Milton W. Davenport.

W. I. KEELER, *Secretary.*

INDIANA SECTION.

The Section met at the office of the State Food and Drug Laboratory, Friday evening, October 13th, with 28 members present.

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Mr. F. R. Eldred, the retiring president, read an address on "The Scope of Pharmaceutical Chemistry."

The following officers were elected: *President*, John White; *Vice-President*, A. D. Thorburn; *Secretary-Treasurer*, A. B. Davis, care Indianapolis Gas Co., Indianapolis; *Executive Committee*, H. E. Jordan, W. D. McAbee, John Short. The reports of the retiring officers were read and approved.

A. D. THORBURN, *Retiring-Secretary*.

UNIVERSITY OF ILLINOIS SECTION.

At the meeting of the Section on October 17th the following papers were presented: "Decomposition of the Nitroso Compounds," by Professor W. A. Noyes and J. A. Coss; "Correlation of the Ionization and Structure in the Aromatic Series," Dr. C. G. Derick.

GRINNELL JONES, *Secretary*.

PHILADELPHIA SECTION.

The first meeting for the season was held in the Engineers' Club, Philadelphia, on October 19th. The following program was presented: "Notes on Some Tests for Distinguishing between Raw and Boiled Milk," by Henry Leffmann. "A Report on the Summer Meeting at Indianapolis," by W. A. Pearson. "The Interpretation of Water Analyses," by D. W. Horn. The attendance, about 72, was unusually large for an opening meeting.

C. S. BRINTON, *Secretary*.

LOUISIANA SECTION.

The fifty-second meeting was held at the Directors' room of the Board of Trade, New Orleans, La., Friday October 20th, at 8.00 P.M.

Dr. E. H. Grant's paper on "Physical Chemistry of Alloys" was followed by brief discussions on chemical topics.

The fifty-third meeting was held at the New Orleans College of Pharmacy, New Orleans, La., Friday, November 17th, at 8.00 P.M.

A paper on "Chemical Equations" was read by Dr. Philip Asher.

GEO. B. TAYLOR, *Secretary*.

SYRACUSE SECTION.

The sixty-ninth regular meeting was held in the Y. M. C. A. building on Friday, October 20th. Dr. Eben H. Archibald, who has just returned from a year of work with Nernst and with Ramsay, spoke on "The Physical Properties of Xenon." Resolutions of appreciation of the life and service of our former Secretary, Dr. William H. McLauchlan, were adopted. A "buffet lunch" was served after the lecture.

The seventieth meeting of the Syracuse Section was held as a joint meeting with the Syracuse Academy of Medicin on November 1st, in Bowne Hall of Chemistry, Syracuse University. Dr. Francis G. Benedict, Director of the Carnegie Nutrition Laboratory of Boston, lectured on "Factors Affecting Changes in Body Weight."

GEO. M. BERRY, *Secretary*.

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CORNELL SECTION.

The sixty-ninth regular meeting was held in Morse Hall, Friday, October 20th, at 8.00 P.M.

Prof. Chas. L. Parsons, Chief Mineral Chemist, Bureau of Mines, gave the address of the evening: "Mineral Wastes—The Chemists' Opportunity."

The November meeting was held on Monday night, November 13th, at 8.00 P.M. in Morse Hall.

The program consisted of the following reports: "Pressure-Concentration-Isotherms in the System, Ammonia-Hydronitric Acid," A. E. Houlehan. "Tensil Strength of Electrolytic Copper," Dr. C. W. Bennett. "The U. S. Bureau of Chemistry," Dr. D. S. Pratt. "The Land Show," Prof. G. W. Cavanaugh.

F. E. RICE, *Secretary.*

CALIFORNIA SECTION.

The fifty-ninth meeting was held on Saturday evening, October 21st, at 8 o'clock, at Bergez-Franks' Café, preceded by the usual dinner. The paper of the evening, "The Elimination of Sulfur Dioxide from Smelter Fumes," was presented by Dr. S. W. Young, of the Leland Stanford Jr. University.

The following officers were elected for the coming year: *Chairman*, F. T. Green; *Vice-Chairman*, T. J. Wrampelmeier; *Secretary-Treasurer*, B. S. Drake, 5930 Colby St., Oakland, Calif.; *Councilors*, W. C. Blasdale and R. E. Swain.

CHARLES S. ASH, *Retiring-Secretary.*

KANSAS CITY SECTION.

The Section met at the Y. M. C. A. Building, Kansas City, Mo., Saturday, October 21st. Dinner was served at six o'clock, after which the following program was given:

"The Relation of Chemistry Abroad to Chemistry in America," F. B. Dains. "The Schools of Germany," J. A. Radke.

The next meeting was held in Lawrence, Saturday morning, November 11th, at 10.00 o'clock, in the Chemistry Building, University of Kansas. Dr. Louis Kahlenberg, of the University of Wisconsin, lectured on "Replacement of the Metals by One Another in Non-aqueous Media." Dinner was served after the Saturday morning lecture.

E. A. WHITE, *Secretary.*

RHODE ISLAND SECTION.

The regular meeting was held at the University Club, on Thursday evening, October 26th, preceded by dinner at 7 o'clock.

The speaker for the evening, Dr. J. H. Appleton, of Brown University, gave an address on "The Indigoids."

ALBERT W. CLAFLIN, *President.*

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MINNESOTA SECTION.

The 34th regular meeting was held in the Chemical Laboratory of the University of Minnesota, on Friday evening, October 27th, with 51 in attendance. The minutes of the three previous meetings were read and approved. Communications from the Secretary of the Society and the Secretary of the Chicago Section were read. The address of the evening was on "Some European Chemical Laboratories," by G. B. Frankforter. (Illustrated with lantern slides.)

The next meeting was held in the Chemical Laboratory of the University of Minnesota, Friday evening, November 17th, at 8.00 P.M.

The following program was presented: "A Reaction of Alkyl Iodides on Some Phenol Silver Salts," W. H. Hunter. "Modern Methods of Color Photography," A. H. Nietz. (Illustrated by lantern slides.)

FRANCIS C. FRARY, *Secretary.*

UNIVERSITY OF MICHIGAN SECTION.

The October meeting was held Tuesday, October 31st, at 4.30, in the Chemical Building. Dr. S. C. Lind delivered an address on "The Chemists' Interest in Radioactivity."

WILLIAM GABB SMEATON, *Secretary.*

SECTION OF WESTERN NEW YORK.

A meeting was held November 7th, at 8.30 P.M., in the lecture hall, Buffalo University, Buffalo, N. Y., with 28 members present.

Papers were presented by N. W. Shed, "Chemistry of the Foundry Industry," and R. Taggesell, "Recent Progress in Dyestuff Chemistry."

Informal dinner at the German-American Hotel preceded the meeting.

WALTER WALLACE, *Secretary.*

WASHINGTON SECTION.

The two hundred and ninth regular meeting was held in the assembly room of the Cosmos Club, Thursday, November 9th, at 8.00 P.M.

No formal paper was presented, but the Entertainment Committee provided a smoker after the election.

H. S. BAILEY, *Secretary.*

NORTHEASTERN SECTION.

A joint meeting of the New England Section of the Society of Chemical Industry with the Northeastern Section of the American Chemical Society was held at the Lowell Building of the Massachusetts Institute of Technology, at 8.00 P.M., Friday, November 10th, preceded by the usual dinner at the Boston Athletic Club.

Dr. L. H. Baekeland gave an interesting address on "Recent Developments in Bakelite" with demonstration.

W. K. LEWIS, *Secretary.*

NEW YORK SECTION.

The second regular meeting was held in conjunction with the Society

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of Chemical Industry and the American Electrochemical Society in Rumford Hall on November 10th, A. C. Langmuir in the chair.

The evening was devoted to a Symposium on Fuel Economy, which included the following papers: J. W. Loveland, "Some Attempts at Economy in Steam Making." Chas. E. Lucke, "Fuel Gasification for Industrial Purposes." Ed. A. Uehling, "A Continuous Carbon Dioxide and Temperature Recorder and Its Application to Combustion Efficiency." Chas. A. Davis, "Is Peat an Important Fuel in America?" Horace C. Porter and F. K. Ovitz, "Deterioration and Spontaneous Heating of Coal in Storage."

C. M. JOYCE, *Secretary.*

CLEVELAND SECTION.

The November meeting was held November 13th in the Chemical Lecture Room of the Western Reserve Medical College.

The program for the evening consisted of a Symposium on Cleveland's Water Supply including the following papers: "Contamination of Water Supplies, Sources and Remedies," by Dr. J. G. Spenzer. "The Present Condition of Cleveland's Water Supply," by Dr. R. G. Perkins. "Some European Water Supplies and Sewage Disposal," by Dr. Hippolyte Gruener. "Rational Consideration of Water Purification," by Dr. P. L. Hobbs.

W. R. VEAZEY, *Secretary.*

CHICAGO SECTION.

The November meeting was held at Kent Laboratory, University of Chicago, on Friday evening, November 17th, at 8.00 P.M., preceded by an informal dinner. 165 attended the meeting and 54 the dinner.

The address for the evening on "Radioactivity and the Nature of Matter," a review of our present knowledge of the subject of Radioactivity, together with a discussion of the modern theory of the electrical nature of matter, and especially of the metallic state, was presented by Prof. Herbert N. McCoy.

D. K. FRENCH, *Secretary.*

COLUMBUS SECTION.

A meeting of the Section was held May 10th, in Chemical Hall, Ohio State University. Prof. Alexander Smith, President of the American Chemical Society, addressed the Section upon Vapor and Dissociation Pressures. Prof. Smith illustrated his lecture by plates showing the work and results obtained by himself and Prof. Menzies upon various subjects such as mercury, water, ammonium chloride and calcium carbonate, with very wide ranges of temperatures emphasizing the fact that these determinations now approximate atomic weight accuracy

JAMES R. WITHROW, *Secretary.*

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THE EFFECT OF SALTS UPON THE SOLUBILITY OF OTHER SALTS, V. THE SOLUBILITY OF UNIBIVALENT SALTS IN SOLUTIONS OF SALTS OF DIFFERENT TYPES.

BY WILLIAM D. HARKINS.

Received August 28, 1911.

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Bivalent Ion Whose Own Intermediate Ion is Present in Large Proportion. 26. Summary of Papers V, VI and VII on Unibivalent Salts.

1. Introduction.

There has been a marked tendency among chemists to apply the solubility-product principle, usually together with the principle of the constancy of the concentration of the unionized part, to unibivalent salts, even though there are several cases in the literature in which it is clearly shown that the addition of certain salts with a common ion may cause only a slight lowering, or even an increase in the solubility. Even the investigators who have obtained the data which show this fact regard the solubility-product principle as true, and seek to harmonize their data with the theory by the assumption of a *specific* double salt or intermediate ion. In no case has there been a suggestion that the effect is a general one, or that double salts or intermediate ions occur other than with certain specific salts, which are therefore supposed to be abnormal in their behavior. A comparison of the meager existing data[1] suggested that the peculiar effect of the bivalent common ion upon the total solubility may be general instead of specific, and that the deviations may be regular, and therefore due to some common cause or causes. It was the purpose of this research to investigate this point in as general a way as possible, in order to discover if such a regularity exists, and if so, to endeavor to give some explanation of the great apparent deviations from the solubility-product principle.

This investigation was undertaken at the suggestion of Prof. A. A. Noyes, and was carried out at the Mass. Institute of Technology with the aid of a grant made to him by the Carnegie Institution of Washington.

The substances used for the solubility determinations were silver sulfate, barium bromate, and lead chloride; and their solubilities were determined at 25° in water, and in solutions of salts of as many different types as possible, both of those with no common ion and of those with a common ion. The conductances and densities of all of the simple solutions and of the mixtures were measured. In the calculations the atomic weights for 1910 were used, and all weighings were corrected for air-buoyancy.

2. Preparation of Salts and Solutions.

All of the salts used in this investigation were finally purified by recrystallization from conductivity water, with a maximum specific conductance, in the bottles in which it was stored, of 0.8×10^{-6}.

Silver Sulfate.—This salt was made by three methods, and all of these methods gave a salt of the same solubility, except where the salt had turned dark during recrystallization. This darkening always resulted in an increase in solubility. All of the silver sulfate was recrystallized and kept in the dark, both before and during the solubility determinations, in order to prevent darkening by the action of light.

[1] See the first article of this series, Noyes and Bray, THIS JOURNAL, 33, 1647-9.

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(1) A sample of Eimer and Amend's silver sulfate was recrystallized once from conductivity water.

(2) The salt was obtained from Merck & Co., and was dissolved at 300° in an excess of concentrated sulfuric acid. The silver acid sulfate[1] which separated out on cooling was washed with water until the washings were neutral to litmus, and the silver sulfate thus obtained was recrystallized from conductivity water.

(3) The silver sulfate was first reduced by an alkaline saccharose solution, the silver dissolved in dilute nitric acid, evaporated and silver nitrate precipitated by concentrated nitric acid. The silver nitrate was washed, dissolved in water, and silver sulfate precipitated by adding sulfuric acid. The silver sulfate thus formed was purified by recrystallization from water until the solution of the salt was alkaline to litmus and acid to rosolic acid.

Potassium Nitrate.—This salt was purified by seven crystallizations from water and was dried at 160° in a current of dry air.

Silver Nitrate.—Kahlbaum's silver nitrate was recrystallized from water. A stock solution was made up and analyzed by precipitation with dilute hydrochloric acid.

Magnesium Nitrate.—This salt was purified by two methods as follows: (1) Kahlbaum's magnesium nitrate was dissolved in water, and boiled with magnesium carbonate formed by precipitating a magnesium nitrate solution by pure dilute sodium carbonate solution, the solution was filtered, the filtrate made acid with nitric acid and partly evaporated, and the salt separated by cooling and filtration. This salt was then recrystallized from water until it was alkaline to litmus and acid to rosolic acid. A stock solution was made up, and its concentration determined by adding sulfuric acid to a portion of the solution and evaporating in a platinum crucible. The precipitate was ignited and weighed as anhydrous magnesium sulfate.

(2) Merck's magnesium nitrate was dissolved in concentrated nitric acid, the residue filtered off, and the salt crystallized by evaporation and cooling. This salt was recrystallized from water until it was alkaline to litmus and acid to rosolic acid. A stock solution was made up, and analyzed by evaporation with sulfuric acid.

Potassium Sulfate.—This was obtained by recrystallizing from water a sample of the salt obtained from Kahlbaum, and by drying at low redness.

Magnesium Sulfate.—Kahlbaum's magnesium sulfate was recrystallized twice from water. A stock solution was made up, and analyzed by evaporation and weighing as magnesium sulfate.

Barium Bromate.—This salt was made by a double decomposition of Kahlbaum's barium chloride and potassium bromate in dilute solution. It was recrystallized from water until it was entirely free from chloride.

Potassium Bromate.—A sample of Kahlbaum's potassium bromate was recrystallized twice from water. The salt was dried at 130° and the solutions made by weighing out the salt. The solutions were also analyzed by precipitation as silver bromide after a reduction by hydrazine, according to the method described later.

Barium Nitrate.—A sample of Kahlbaum's barium nitrate was recrystallized twice from water and dried for 24 hours in a current of dry air at 135°. The solutions were made by weighing out the dry salt.

Lead Nitrate.—Kahlbaum's lead nitrate was recrystallized from water containing a slight amount of nitric acid. The salt was heated at 100° for 6 hours, and at 130° for 12 hours in a current of dry air. The salt when dissolved gave a solution acid to rosolic acid and alkaline to litmus.

Lead Chloride.—This salt was precipitated by pure hydrochloric acid from a dilute

[1] Schultz, *Pogg. Ann.*, 133, 143 (1868).

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solution of Eimer and Amend's lead nitrate. It was recrystallized from water until the salt became neutral. Stock solutions were made and analyzed by precipitation as silver chloride.

3. Methods of Analysis.

Silver.—The concentration of solutions of silver salts was determined in every case by precipitation as silver chloride. Enough solution was taken to give a precipitate of more than 1 gram in weight, and then diluted to approximately 0.05 normal. This solution was then added to a sufficient excess of 0.05 normal hydrochloric acid solution to give a final solution about 0.005 normal with respect to hydrochloric acid. The solution was allowed to stand cold, and in the dark, for 24 hours. It was then filtered through a weighed Gooch crucible, made of platinum, which had an asbestos mat protected by a perforated plate of platinum. The crucibles were previously brought to a constant weight by gradually heating up to 160°, and then heating at this temperature over night. The precipitate was washed with about a liter of 0.005 normal hydrochloric acid and then dried for 4 hours at 100° and for 12 hours at 160°. According to Richards[1] the solubility of silver chloride in a solution containing an excess of hydrochloric acid with some sodium nitrate amounts to about 0.03 mg. per liter. The concentration of the excess of hydrochloric acid is not given, but it is certain from an application of solubility-product principle that the solubility of silver chloride had no influence upon the results.

4. The Analysis of Bromates.

Bromate.—The concentration of barium bromate and potassium bromate solutions was determined by precipitation as silver bromide after a reduction by hydrazine. The solution was reduced in a half-liter bottle of the form devized by Baxter[2] and by a method somewhat similar to that used by him for the reduction of iodic acid. To the solution nearly twice the theoretical quantity of hydrazine hydroxide was added, and then nitric acid was dropped in slowly through a thistle tube which extended to the bottom of the bottle. This acid solution was heated to 60° for some time and then allowed to cool, and the determination completed by adding the diluted bromide solution to a dilute silver nitrate solution.

The results of this method were checked by analyzing solutions of potassium bromate made by weighing out the dry salt. The salt used was dried at 130°, but its weight was corrected by the amount of moisture given off by a part of the sample on heating for 19 hours at 165°, and 13 hours at 230°. The concentration of the potassium bromate solutions

[1] "Revision of the Atomic Weights of Sodium and Chlorine," Richards and Wells, *Carnegie Publications*, 1905.

[2] THIS JOURNAL, 31, 209 (1909).

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was also determined by titration against a thiosulfate solution which was standardized by Prof. W. C. Bray against pure iodine, pure copper sulfate, and pure potassium iodide. The latter solution was standardized by precipitation as silver iodide. In all cases the agreement was satisfactory. The analysis of the potassium bromate solutions by reduction with hydrazine and precipitation as silver bromide gave results from 0.02 to 0.03 per cent. lower than those obtained from the weight of the potassium bromate. The method is undoubtedly by far the most accurate one yet devized for the analysis of bromates.

Chloride or Bromide.—Chloride and bromide were determined by adding to solutions containing these radicals an equivalent quantity of very dilute silver nitrate solution, allowing to stand over night, and adding a slight excess of silver nitrate the next day.[1] The precipitates were washed with very dilute silver nitrate solution and then with 100 cc. water made slightly acid by nitric acid. No correction was made for the amount of silver chloride dissolved by the wash water, but this was small, and in the case of the bromide it was practically negligible.

5. Experimental Methods.

The solubility was determined by rotating, for about 24 hours, about 20 grams of the salt with water or the solution of a salt in a 250 cc. glass-stoppered "resistenz" glass bottle, the stopper of which was sealed in with paraffin. The temperature of the thermostat was measured by a thermometer, which was frequently compared with a Baudin thermometer which had been certified by the Bureau of Standards at Washington, and was kept at 25° ± 0.01 by means of a large regulator filled with mercury. For each determination, saturation was approached both from under-saturation and supersaturation. In order to supersaturate the solution it was first saturated at a temperature of about 40° and then allowed to cool to the temperature of the thermostat.

The solutions were filtered in the thermostat by forcing them by means of air pressure through a thin inverted submerged asbestos filter which was held in a glass tube between two perforated platinum disks. The first 50 cc. of solution which was passed slowly through the filter, was rejected, in order to prevent errors from adsorption, and the remainder of the filtrate was used for analyses, conductivity measurements and density determinations.

The conductivity measurements were made in the usual way with a Kohlrausch slide-wire bridge carefully standardized. The apparatus was that used in this laboratory by Franklin L. Hunt[2] for the determination of the conductance of certain aqueous solutions.

[1] Richards, "Researches Concerning Atomic Weights," *Carnegie Publication*, page 17 (1907).

[2] THIS JOURNAL, 33, 796 and 783 (1911).

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6. Solubility of Silver Sulfate in Water.

Ten determinations were made of the solubility in water, and the results of the measurements are given in Table I. In making up the average, measurements one to four were rejected because the salt darkened slightly, and nine and ten, because the salt was slightly acid with sulfuric acid. All of the bottles were protected from the action of light by being enclosed in covers of black rubber, but there seemed to be a slight darkening and a resultant increase of solubility whenever the salt had been only very slightly darkened during the recrystallization from hot water. It was found that even when recrystallized in the dark after a previous heating to 300° with concentrated sulfuric acid to insure the absence of organic matter the salt darkened if it was heated in water for any considerable time after it had become perfectly neutral. This darkening seemed to proceed much more rapidly as soon as darkening once began, but a slight amount of sulfuric acid served to prevent this action even in the hot solution. The salt used in all of this work was perfectly white except that used in the first four experiments. To prevent darkening the solution was heated as short a time as possible during the recrystallization from water.

Conductivity measurements were made upon three of the solutions, but it was considered better to take the results obtained from solutions which had not been rotated in the thermostat. A complete series of conductivity measurements upon the silver sulfate used in this work was made by Franklin L. Hunt. However, the two sets of results show that the equivalent conductance was practically the same for the two series of measurements, and therefore the darkening seems to have had no appreciable effect upon the conductivity of the solution.[1]

TABLE I.—SOLUBILITY OF SILVER SULFATE IN WATER AT 25°.

(Concentrations in milliequivalents per liter.)

	Conc. Ag_2SO_4.	Spec. cond. × 10^3.	Equiv. cond.	Density 25°/4°.
1	53.58	5.232	97.65[1]	1.0052
2	53.74(s)[2]	5.247	97.64	
3	53.74(s)	5.257	97.83	
4	53.62			
5	53.50			
6	53.48			
7	53.58(s)			
8	53.52(s)			
9	53.62(s)			
10	53.58(s)			

Mean of best determinations (5, 6, 7, and 8) = 53.52 milliequivalents per liter = 8.344 grams per liter.

[1] The average value of the equivalent conductance of the saturated solution obtained by Hunt was 97.7.

[2] (s) denotes that equilibrium was approached from the side of supersaturation.

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The final value for the solubility at 25°, 0.02676 moles per liter, is 4.1 per cent. higher than that obtained by Drucker,[1] 0.0257 moles per liter, and 0.86 per cent. lower than that obtained by Swan,[2] 0.02699 moles per liter.

7. The Solubility of Silver Sulfate in Solutions of Magnesium Nitrate, Potassium Nitrate, Magnesium Sulfate, Potassium Sulfate, Silver Nitrate, Potassium Acid Sulfate, Sulfuric Acid and Nitric Acid.

The results of the solubility determinations in solutions of potassium nitrate, magnesium nitrate, potassium sulfate, magnesium sulfate, and silver nitrate are given in Table II. In this table columns one to three refer to the salt solution which was used in the solubility determination,

TABLE II.—SOLUBILITY OF SILVER SULFATE IN SALT SOLUTIONS AT 25°.

(Concentrations in milliequivalents per liter.)

Salt solution.			Mixture.					
No.	Salt.	Conc. salt.	d. 25°/4°.	Solubility Ag_2SO_4.	Mean solubility.	Solubility grams per liter.	Sp. cond. $\times 10^3$.	d. 25°/4°.	Conc. added salt in mix.
	None	0.00			53.52	8.344	8.344		
11	KNO_3	24.914	0.9986	57.64				1.0072	24.903
12				57.68(s)			8.402		
13				57.76(s)					
14				57.72	57.70	8.996			
15		49.774	1.0002	61.06			11.403	1.0092	49.749
16				61.12(s)					
17				61.20(s)					
18				61.18					
19				61.14(s)					
20				61.08(s)	61.13	9.531			
21		99.87	1.0034	66.92			17.204	1.0034	99.81
22				66.90			17.251		
23				66.88(s)					
24				66.94					
25				67.00(s)	67.93	10.435			
26	$Mg(NO_3)_2$	24.764	0.9985	59.44			7.373	1.0073	24.750
27				59.44					
28				59.44(s)					
29				59.44(s)	59.44	9.267			
30		49.595	0.9999	64.28			9.522	1.0094	49.569
31				64.38(s)			9.529		
32				64.34(s)	64.32	10.029			
33		99.46	1.0026	72.70			13.750	1.0133	99.40
34				72.68(s)					
35				72.70(s)	72.70	11.334			
36	$AgNO_3$	24.961	1.0007	39.08			6.497	1.0065	24.96
37				39.10(s)	39.09	6.095			
38		49.86	1.0044	28.44			8.125	1.0084	49.84

[1] *Z. anorg. Chem.*, 28, 362 (1901).

[2] "Chemistry Thesis," Mass. Institute of Technology (1899).

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TABLE II (*continued*).

Salt solution.			Mixture.					
No.	Salt.	Conc. salt.	*d.* 25°/4°.	Solubility. Ag_2SO_4	Mean solubility	Solubility grams per liter.	Sp. cond. × 10^3.	*d.* 25°/4°.	Conc. added salt in mix.
39				28.46(*s*)	28.45	4.487	8.123		
40		99.61	1.0112	16.94			12.122	1.0137	99.60
41				16.98(*s*)	16.96	2.644	12.125		
42	K_2SO_4	25.024	(0.9989)	(50.80)[1]			7.517	1.0064	25.015
43				(51.20)[1]			7.535		
44				50.66					
45				50.66(*s*)	50.66	7.899			
46		50.044	1.0006	49.34			9.806	1.0079	50.025
47				49.36(*s*)	49.35	7.694	9.807		
48		100.00	(1.0041)	(48.26)[1]			14.396	1.0112	99.96
49				(48.06)[1]			14.383		
50				48.04					
51				48.04(*s*)	48.04	7.490			
52		200.03	1.0110	48.26			23.187	1.0180	199.96
53				48.34(*s*)	48.30	7.531	23.190		
54	$MgSO_4$	20.022	0.9984	52.18			6.118	1.0061	20.014
55				52.24(*s*)	52.21	8.140	6.119		
56		50.069	1.0002	50.92			7.371	1.0079	50.059
57				50.94(*s*)	50.93	7.941	7.370		
58		100.04	1.0032	49.96			9.410	1.0105	99.96
59				49.94(*s*)	49.95	7.740	9.409		
60		200.05	1.0092	49.60			13.242	1.0164	199.87
61				49.60(*s*)	49.60	7.733	13.241		

TABLE II B.—THE SOLUBILITY OF SILVER SULFATE IN SOLUTIONS OF ACIDS AND SALTS ACCORDING TO SWAN.[2]

Acid or salt added.	Conc. in milliequivalents.	Solubility (milliequivalents).	Fractional conc. added acid or salt	Fractional solubility.
HNO_3	0.0	53.98	0.0	1.0
	15.89	59.86	0.294	1.110
	31.78	65.32	0.588	1.211
	63.57	75.90	1.177	1.406
H_2SO_4	0.0	53.98	0.0	1.0
	29.02	54.88	0.538	1.017
	58.02	55.64	1.075	1.031
	105.26	56.82	1.951	1.057
$KHSO_4$	0.0	53.98	0.0	1.0
	52.64	52.18	0.976	0.967
	105.26	51.76	1.951	0.959
K_2SO_4	0.0	53.98	0.0	1.0
	27.18	50.90	0.504	0.943
	54.34	49.30	1.006	0.914

[1] The numbers in parentheses were not used in determining the average since they are the results obtained in experiments where the silver sulfate darkened perceptibly.

[2] Clifford M. Swan, "Chemistry Thesis," Mass. Inst. Tech., 1899.

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and columns 4 to 9 give data concerning the mixture after equilibrium has been established. Column nine gives the concentration of the added salt corrected for the change of volume which takes place during the dissolving of the silver sulfate.

In Table II B are given the results of measurements upon the solubility of silver sulfate in solutions of nitric acid, sulfuric acid, potassium acid sulfate and potassium sulfate. The data are taken from an unpublished thesis by Clifford M. Swan.

8. The Solubility of Barium Bromate in Water and in Solutions of Potassium Nitrate, Magnesium Nitrate, Barium Nitrate and Potassium Bromate.

The solubility of barium bromate in milliequivalents per liter is given in Table III.

TABLE III.—SOLUBILITY OF BARIUM BROMATE IN WATER AT 25°.

Solubility.	Conductance $\times 10^3$.	Equivalent cond.	Density 25°/4°.
40.20(*s*)	3.664	91.1	1.0038
40.14			
40.18			
40.18(*s*)			

Mean = 40.18 = 0.793 gram to 100 grams solution.

TABLE IV.—SOLUBILITY OF BARIUM BROMATE IN SOLUTIONS OF SALTS AT 25°.
(Concentrations in milliequivalents per liter.)

Salt solution.				Mixture.					
No.	Salt.	Milli-equiv. conc.	*d.* 25°/4°.	Solubility Ag_2SO_4 in milli-mols.	Solubility, grams per liter. Mean.		Sp. cond. $\times 10^3$.	*d.* 25°/4°.	Conc. salt.
	None	0.00		40.18	40.18			1.0038	0.00
100	KNO_3	25.018	0.9985	43.88			6.783	1.0059	24.988
101				43.84(*s*)	43.86	8.62	6.784		
102		50.032	(1.003)	47.02			9.756	1.0081	50.02
103				47.04(*s*)	47.03	9.91	9.737		
104		99.97	1.0033	52.12			15.452	1.0120	99.77
105				52.14(*s*)	52.13	10.25	15.451		
106	$Ba(NO_3)_2$	25.018	1.0003	36.70			5.643	1.0059	24.978
107				36.84(*s*)	36.77	7.221			
108		50.039	1.0025	34.72			7.597	1.0083	49.990
109				34.76(*s*)	34.74	6.83	7.596		
110		99.97	1.0073	32.60			11.325	1.0132	99.92
111				32.66(*s*)	32.63	6.415	18.100		
112		199.95	1.0183	30.96			18.097	1.0233	199.54
113				30.94(*s*)	30.95	7.085		1.0046	24.970
114	$KBrO_3$	24.988	(1.0001)	26.52					
115				26.54(*s*)	26.53	5.216			
116		49.971	(1.0031)	17.38			6.974	1.0062	49.956
117				17.36(*s*)	17.37	3.415	6.973		
118		99.85	1.0093	8.82			11.309	1.0109	99.84
119				8.70(*s*)	8.76	1.72	11.308		
120	$Mg(NO_3)_2$	100.00		52.54				1.0114	
121				52.60(*s*)	52.57	8.196			

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The solubility was determined by precipitating as silver bromide, after reducing with hydrazine, and is 0.63 per cent. higher than that found by Trautz and Anschütz[1] (0.788 gram). According to the analyses given in their article the solid phase has the composition $Ba(BrO_3)_2H_2O$.[1]

The solubility of barium bromate in salt solutions is given in Table IV.

9. The Solubility of Lead Chloride in Water and in Solutions of Salts.

The solubility of lead chloride in water and in solutions of lead nitrate is given in Table V.

TABLE V.—SOLUBILITY OF LEAD CHLORIDE IN WATER AND IN SOLUTIONS OF LEAD NITRATE.

(Concentrations in milliequivalents per liter.)

Salt solution.				Mixture.					
No.	Salt.	Equiv. conc.	d. 25°/4°.	Solubility $PbCl_2$.	Solubility, grams per liter. Mean.	Solubility, grams per liter.	Sp. cond. $\times 10^3$.	d. 25°/4°.	Conc. salt.
118	Water			77.76					
119				77.76	77.76			1.0069	
120	$Pb(NO_3)_2$	20.020	(1.0008)	76.74					
121				76.76	76.75	10.67		1.0095	19.980
122		50.063	(1.0045)	76.64					
123				76.64	76.64	10.65		1.0139	50.003
124		99.66	1.0119	77.98			13.124		99.49
125				77.98	77.98	10.84	13.124	1.0210	
126		200.0		83.20[2]					

In Table VI are given the mean results on the solubility of lead chloride as obtained by A. A. Noyes.[3]

TABLE VI.—SOLUBILITY OF LEAD CHLORIDE AT 25° ACCORDING TO A. A. NOYES.

(Concentrations in milliequivalents per liter.)

Salt added.		50.	100.	200.
HCl	77.70	47.86	32.43	19.27
KCl	...	48.2	34.1	21.9
$MgCl_2$	...	50.3	35.0	...
$CaCl_2$	...	50.3	35.5	21.9
$MnCl_2$	...	50.1	34.9	21.7
$ZnCl_2$	...	...	...	22.0
$CdCl_2$	...	60.1	48.1	35.5
$HgCl_2$	...	...	99.2	...
$Pb(NO_3)_2$	...	...	...	83.2

The mean values for the solubility of silver sulfate, barium bromate, and lead chloride, together with the results of A. A. Noyes upon the solubility of lead chloride,[4] and of Abegg and Spencer on the solubility

[1] *Z. physik. Chem.*, 56, 240 (1906).

[2] No. 126 is the mean of two results obtained by A. A. Noyes, *Z. physik. Chem.*, 9, 629 (1892).

[3] *Loc. cit.*, 623–9.

[4] *Z. physik. Chem.*, 9, 629 (1892).

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of thallium oxalate,[1] have been brought together in Table VII. The column headed "Fractional conc. salt" gives the values of the ratio.[2]

$$\frac{\text{Equivalent concentration of added salt}}{\text{Equivalent solubility of saturating salt in water,}}$$

while the column headed "Fractional solubility" gives the values of the ratio

$$\frac{\text{Solubility of salt in salt solution}}{\text{Solubility of salt in water.}}$$

These ratios will be used for the plotting of curves, which will be given in the seventh paper of this series.

TABLE VII.—MEAN VALUES FOR THE SOLUBILITY OF SALTS IN SOLUTIONS OF SALTS.

Salt added.	Milli-normal conc. salt solution.	Solubility in milli-moles.	Fractional conc. added salt.	Fractional conc. solubility.	Solubility in grams per liter.	Density solution 25°/4°.
		Solubility of Silver Sulfate.				
KNO_3	0.0	26.76	0.0	1.0	8.344	1.0052
	24.903	28.85	0.466	1.078	8.996	1.0072
	49.749	30.56	0.930	1.142	9.531	1.0092
	99.81	33.96	1.866	1.250	10.435	1.0034
$Mg(NO_3)_2$	0.0	26.76	0.0	1.0	8.344	1.0052
	24.750	29.72	0.463	1.112	9.267	1.0073
	49.569	32.16	0.926	1.202	10.029	1.0094
	99.40	36.35	1.857	1.358	11.334	1.0133
$AgNO_3$	0.0	26.76	0.0	1.0	8.344	1.0052
	24.96	19.55	0.466	0.7075	6.095	1.0065
	49.84	14.22	0.932	0.528	4.428	1.0084
	99.60	8.48	1.861	0.313	2.644	1.0137
K_2SO_4	0.0	26.76	0.0	1.0	8.344	1.0052
	25.015	25.33	0.468	0.9475	7.899	1.0064
	50.025	24.67	0.936	0.922	7.694	1.0079
	99.96	24.02	1.878	0.898	7.490	1.0112
	199.96	24.15	3.740	0.9025	7.521	1.0180
$MgSO_4$	0.0	26.76	0.0	1.0	8.344	1.0052
	20.014	26.10	0.375	0.976	8.140	1.0061
	50.059	25.46	0.936	0.952	7.941	1.0079
	99.96	24.97	1.868	0.934	7.788	1.0105
	199.87	24.80	3.713	0.927	7.733	1.0164

[1] *Z. anorg. Chem.*, 46, 406 (1905).

[2] Throughout these papers certain terms will be used which are not accurate except as defined here. The term "added salt" will be used to denote the salt originally present in the standard solutions in which other salts were dissolved later. By the "saturating salt" is meant the salt which is present in a solution in contact with the solid phase, and also in equilibrium with it. These short terms are much more convenient than the accurate explanation, and the effect is the same as if the "saturating salt" were first dissolved to form its saturated solution, and then the "added salt" added in the solid form in the correct proportions and the whole rotated until equilibrium is reached. Of course this latter method could not be recommended as a method for accurate work, but it is often of use in obtaining approximate results quickly—for example in teaching solubility principles to students of qualitative analysis.

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TABLE VII (*continued*).

Salt added.	Milli-normal conc. salt solution.	Solubility in milli-moles.	Fractional conc. added salt.	Fractional conc. solubility.	Solubility in grams per liter.	Density solution 25°/4°.
		Solubility of Barium Bromate.				
$Mg(NO_3)_2$	0.0	20.09	0.0	1.0	7.93	..
	100.0	26.28	2.490	1.308	8.196	1.0114
KNO_3	0.0	20.09	0.0	1.0	7.93	1.0038
	24.988	21.93	0.622	1.092	8.62	1.0059
	50.02	23.01	1.246	1.146	9.91	1.0081
	99.77	26.06	2.482	1.297	10.25	1.0120
$Ba(NO_3)_2$	0.0	20.09	0.0	1.0	7.93	1.0038
	24.978	18.38	0.623	0.915	7.22	1.0059
	49.99	17.37	1.246	0.865	6.683	1.0083
	99.92	16.31	2.486	0.812	6.415	1.0132
	199.54	15.47	4.978	0.770	7.085	1.0233
$KBrO_3$	0.0	20.09	0.0	1.0	7.93	1.0038
	24.970	13.26	0.624	0.662	5.216	1.0046
	49.956	8.68	1.248	0.433	3.415	1.0062
	99.84	4.38	2.488	0.218	1.72	1.0109
		Solubility of Lead Chloride.				
$Pb(NO_3)_2$	0.0	38.88	0.0	1.0	10.81	1.0069
	19.98	38.37	0.258	0.987	10.67	1.0095
	50.003	38.32	0.644	0.986	10.65	1.0139
	99.49	38.99	1.282	1.003	10.84	1.021
	200.0	41.60	2.572	1.070	11.566	..
KCl[1]	0.0	38.85	0.0	1.0	10.801	..
	50.0	24.10	0.643	0.620	6.70	..
	100.0	17.05	1.286	0.439	4.74	..
	200.0	10.95	2.571	0.282	3.04	..
HCl[1]	0.0	38.85	0.0	1.0	10.801	..
	50.0	23.93	0.643	0.616	6.653	..
	100.0	16.21	1.286	0.417	4.507	..
	200.0	9.63	2.571	0.248	2.677	..

10. The Solubility of Thallium Oxalate[2] in Solution of Salts.

Salt added.	Conc. salt.	Solubility $Tl_2C_2O_4$.	Fractional conc. salt.	Fractional solubility $Tl_2C_2O_4/2$.
None	0	75.36	0.0	1.0
$TlNO_3$	41.14	52.8	0.546	0.701
	79.90	39.0	1.062	0.518
	159.7	25.7	2.120	0.328
$K_2C_2O_4$	0	75.36	0.0	1.00
	99.6	70.2	1.322	0.932
	199.2	71.3	2.645	0.946
	493.4	78.0	6.55	1.036
	977.2	90.12	12.97	1.196
	1957.0	110.72	26.0	1.47

11. Conductance and Ionization of the Salts at 25°.

Conductance measurements upon a number of salts used in this in-

[1] A. A. Noyes, *Z. physik. Chem.*, 9, 629 (1892).

[2] Abegg and Spencer, *Z. anorg. Chem.*, 46, 406 (1905).

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vestigation were made by Mr. F. L. Hunt and the writer, and are given in Tables VIII–XI together with the results of other investigators.[1]

TABLE VIII.—CONDUCTANCE AND IONIZATION OF THE SALTS AT 25°.

Salt.	$C \times 10^3$.	Equivalent conductance. Measured.	H. M. or J.	B. & W.	Final.	100γ.	$\Sigma i \times 10^3$.
KNO_3	0.0	...	..	..	(145.4)[2]	100.0	0.0
	12.5	...	134.9	..	134.9	92.8	11.60
	20.0	...	..	132.5	132.5	91.1	18.24
	25.0	131.1	..	..	131.1	90.2	22.55
	50.0	126.3	126.3	126.1	126.3	86.85	43.43
	100.0	120.4	120.3	120.3	120.4	82.8	82.8
	200.0	113.5	..	..	113.5	78.0	156.0
	300.0	...	..	108.3	108.6	74.5	223.6
K_2SO_4	0.0	...	..	..	(154.8)	100.0	0
	20.0	...	128.1	127.9	128.0	82.5	16.5
	25.0	125.6	..	..	125.6	81.1	20.3
	50.0	118.1	118.15	117.95	118.1	76.3	38.15
	100.0	109.9	109.9	109.8	109.9	71.0	71.0
	200.0	101.4	101.4	..	101.4	65.5	131.0
	300.0	...	..	96.15	96.15	62.1	186.4

TABLE IX.—CONDUCTANCE AND IONIZATION OF THE SALTS.

Salt.	Conc. $\times 10^3$.	Λ_{25} measured.	100γ.	$\Sigma i \times 10^3$.	Λ_{18}. Kohlrausch.	100γ.
$AgNO_3$	0.0	(134.0)	...	..	(115.8)	100.0
	10.0	..	...	..	107.8	93.2
	25.0	120.0	89.6	22.4	..	..
	50.0	115.1	85.9	42.95	99.5	85.9
	100.0	109.1	81.5	81.5	94.33	81.4
	200.0	101.8	75.97	151.94	..	..
$MgSO_4$	0.0	(135)	...	..	(114.4)	100.0
	20.0	78.6	58.2	11.64	67.7	59.2
	50.0	66.0	48.9	24.45	56.9	49.75
	100.0	57.6	42.65	42.65	49.7	43.4
	200.0	50.0	37.05	74.10	43.2	37.8
$Ba(NO_3)_2$	0.0	135.8	...	..	(117.2)	100.0
	20.0	..	...	..	95.7	81.65
	25.0	108.6	80.0	20.0	..	..
	50.0	100.8	74.25	37.12	86.8	74.06
	100.0	91.8	67.6	67.6	78.9	67.3
	200.0	81.8	60.2	120.4	70.2	59.9
$Pb(NO_3)_2$	0.0	141.8	...	..	(122.6)	100.0
	20.0	112.9	79.6	15.9	97.0	79.04
	50.0	101.0	71.2	35.6	86.4	70.4
	100.0	90.5	63.8	63.8	77.3	63.0
	200.0	79.0	55.75	111.5	67.4	54.9

[1] Potassium nitrate, Noyes and Johnston, THIS JOURNAL, 31, 979 (1909). Potassium sulfate, preliminary values obtained by Mr. A. C. Melcher, of this laboratory. Potassium nitrate and potassium sulfate, Bray and Winninghoff, THIS JOURNAL, 33, 1667 (1911).

[2] Values in parenthesis were obtained by extrapolation.

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Λ is the equivalent conductance, 100γ the conductance ratio ($= 100\ \Lambda/\Lambda_o$) $C \times 10^o$ the concentration in milliequivalents, and $1000\Sigma i = 1000\ C\gamma$, the ion concentrations.

Table X gives the results of conductance measurements made by Mr. F. L. Hunt upon a number of the salts used in this investigation.[1] The values of the conductance ratio (100γ) are given in the table, together with extrapolated values enclosed in parentheses.

TABLE X.—PERCENTAGE IONIZATION OF THE SALTS AT 25°.

Concentration at t^o.	$Mg(NO_3)_2$.	$KBrO_3$.
0	100.0	100.0
1	95.2	97.9
2	93.5	96.9
5	90.5	95.2
10	87.6	93.4
20	84.1	90.9
50	78.8	86.7
100	74.4	82.7
200	69.4	78.0

Concentration at t^o.	Ag_2SO_4 25°.	$Ba(BrO_3)_2$ 25°.	$PbCl_2$ 25°.
0	100.0	100.0	100.0
1	94.7	94.7	94.3
2	92.5	92.7	91.5
4	89.3	...	...
5	88.1	89.2	86.3
10	83.6	85.6	80.4
20	77.9	81.1	73.2
40	71.3	75.9	...
50	...	...	62.1
53.74	68.1	...	...
78.2	64.3	...	...
77.54	...	...	56.2
100	(61.7)	(67.93)	
102.63	..	...	
145.4	..	(64.77)	
200	(54.7)	...	
203.6	..	(61.64)	

Through a typographical error four of the equivalent conductances determined for silver sulfate were given incorrectly in the published article. The correct results are as follows, where (s) represents a saturated solution, and (ss) a supersaturated solution:

Equivalent concentration	53.74(s)	71.8(ss)	72.0(ss)	78.2(ss)
Λ at 25°	97.7	94.3	93.5	92.15

Table XI gives unpublished results upon the conductance of potassium chloride as determined in this laboratory by Mr. A. C. Melcher.

[1] THIS JOURNAL, 53, 802 (1911).

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TABLE XI.—CONDUCTANCE AND IONIZATION OF POTASSIUM CHLORIDE AT 25°.

Conc.	Λ_{25} Melcher.	Λ final.	Per cent. ionization.	Σi.
0.....	..	150.6	100.0	..
10.....	141.4	141.4	93.9	9.39
20.....	138.65	138.55	92.0	18.40
50.....	133.65	133.6	88.7	44.35
100.....	129.0	129.0	85.65	85.65
(146).....	..	(126.4)	83.9	122.6
200.....	124.2	124.2	82.47	164.9

12. Classification of Solubility Curves According to Types.

The solubility data presented in Tables I–VII are given in a graphic form in Fig. 1, where the ordinates represent the molal solubility, and the abscissas, the equivalent concentration of the added salts.

An examination of the figure shows that the curves belong to three general types, as follows:

I. These curves represent the change in solubility when a salt with a common univalent ion is added. In this case the solubility decreases very rapidly with increasing concentration of the added salt. All of these curves are of the same form as would be expected from a qualitative application of the solubility-product principle.

II. These curves represent the change in solubility when a salt with a common bivalent ion is added. The solubility of the more soluble salts, lead chloride and thallium oxalates, at first decreases, but quickly passes through a minimum, and then increases as the concentration of the added salt increases. Silver sulfate, a less soluble salt, shows only an extremely slight increase in solubility when the concentration of the added potassium sulfate is increased from 0.1 to 0.2 normal, though it increases much more rapidly at higher concentrations. On the other hand, the least soluble salt investigated, barium bromate, shows a continuous, though slight, decrease of solubility up to a concentration of 0.2 normal for the added salt.

It is remarkable that in the case of the more soluble salts the form of these curves has no resemblance to what would be expected from an application of the solubility-product principle.

13. Increase in the Solubility of an Easily Soluble Unibivalent Salt Caused by the Addition of a Salt with a Common Bivalent Ion.

The curves for this case seem to be determined by two opposing influences: one, most apparent in dilute solutions, exerts a depressing effect upon the solubility, and is undoubtedly due to the action of the common ion; the other, most apparent in concentrated solutions, tends to increase the solubility. This latter effect becomes more and more apparent as the solubility of the unibivalent salt increases, and for very soluble salts masks almost entirely, or even entirely, the effect of the common

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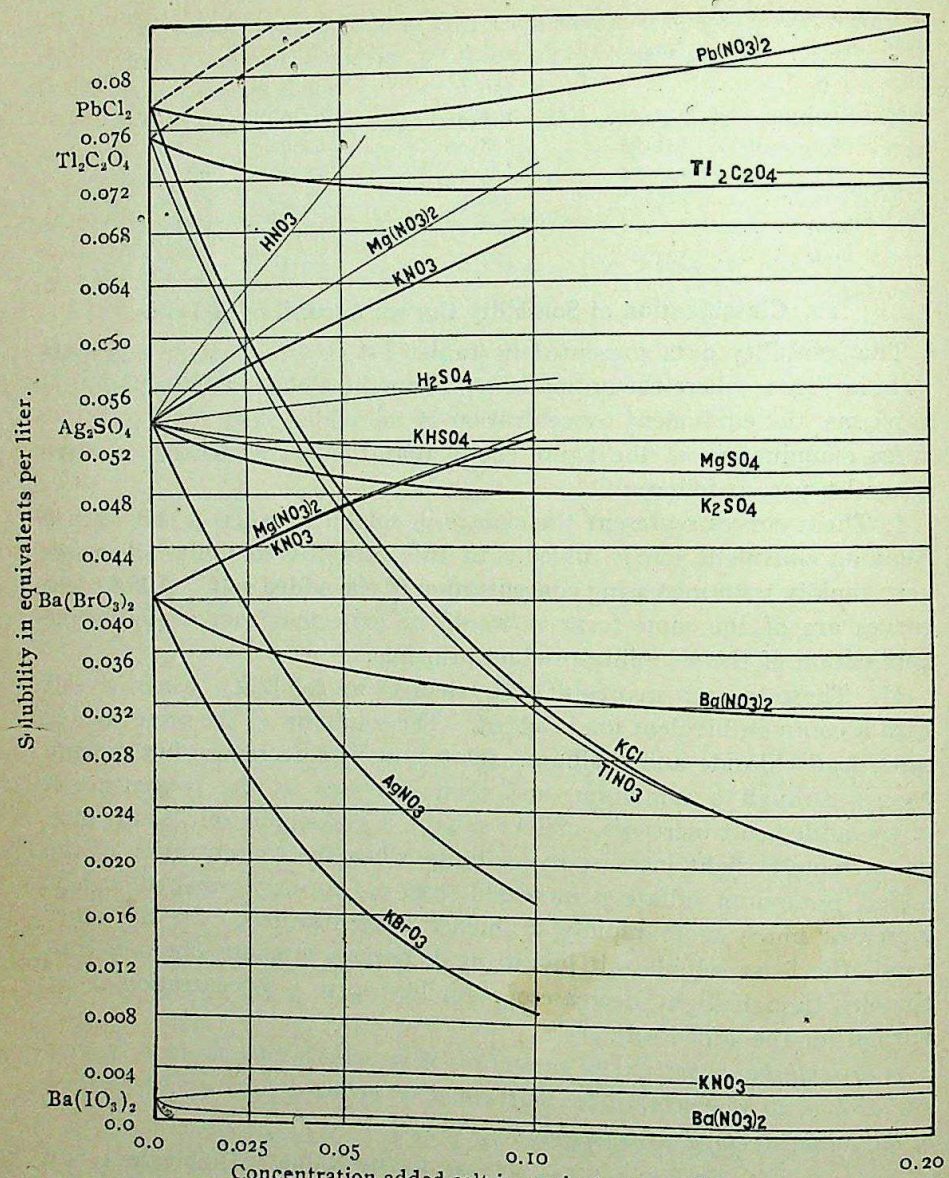

Fig. 1.

ion. This is shown in the case of certain salts investigated by Parsons and Carson[1] and Parsons and Perkins.[2] A much more complete discussion of this case will be found in the seventh article of this series.

There is thus in dilute solutions an effect, which in its direction is what we would expect from the solubility-product principle as the result of the

[1] Parsons and Carson, THIS JOURNAL, 32, 1383 (1910).

[2] Parsons and Perkins, *Ibid.*, 32, 1387.

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presence of the common ion, but it is of an altogether too small magnitude. In more concentrated solutions this effect becomes quickly imperceptible, though it is doubtless true that the common ion is still exerting an effect which is obscured by the influence, whatever it may be, which causes the increase in solubility.

It is interesting to note that potassium acid sulfate decreases the solubility of silver sulfate less than potassium sulfate, and that sulfuric acid, in spite of its common ion, increases the solubility from the start, thus giving a curve similar in this sense to the curves for no common ion, such as those for potassium nitrate and magnesium nitrate; but it lies much below these curves. In position it seems to be then a cross between the curves for common ions and those for no common ion. This was to have been expected, since the intermediate HSO_4^- ion is present in aqueous solutions of potassium acid sulfate and sulfuric acid, but it is remarkable that the curve for potassium sulfate lies so close to the curves for the other two substances in spite of the large amounts of the intermediate ion which solutions of these substances are assumed to contain.[1] The importance of this point will be discussed in the seventh paper of this series.

Incidentally it may be noted that magnesium sulfate does not decrease the solubility of silver sulfate so much as potassium sulfate.

14. Increase of Solubility by Metathesis.

III. These curves represent the change in solubility when salts having no common ion are added. In such cases the solubility increases rapidly with the concentration of the added salt as the result of metathesis. It was found that magnesium nitrate increases the solubility of silver sulfate much more than it is increased by the addition of potassium nitrate. On the other hand magnesium nitrate increases the solubility of barium bromate only very slightly more than it is increased by potassium nitrate. This difference seems peculiar until we consider the metatheses in the different cases. The cause of the difference is largely the different degrees of ionization of the salts in the following metatheses:

$$(1)\ \underset{77.9}{Ag_2SO_4} + \underset{84.1}{Mg(NO_3)_2} \rightleftarrows \underset{59.2}{MgSO_4} + \underset{90.8}{2AgNO_3}.$$

$$(2)\ \underset{77.9}{Ag_2SO_4} + \underset{91.1}{KNO_3} \rightleftarrows \underset{82.6}{K_2SO_4} + \underset{90.8}{2AgNO_3}.$$

$$(3)\ \underset{81.1}{Ba(BrO_3)_2} + \underset{84.1}{Mg(NO_3)_2} \rightleftarrows \underset{82}{Mg(BrO_3)_2} + \underset{81.8}{Ba(NO_3)_2}.$$

$$(4)\ \underset{81.1}{Ba(BrO_3)_2} + \underset{91.1}{KNO_3} \rightleftarrows \underset{90.9}{KBrO_3} + \underset{81.8}{Ba(NO_3)_2}.$$

[1] This is not an exceptional case, since similar results were obtained by Noyes and Stewart with thallous sulfate in the presence of sodium sulfate, sodium acid sulfate and sulfuric acid, Article II, C of this series. THIS JOURNAL, 33, 1663 (1911).

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The figures given under the formulas represent the percentage ionization of the single salts in aqueous solution at a concentration of 20 milliequivalents per liter. These figures show that the ionization of the salts on the two sides of equations (2), (3) and (4) are almost exactly balanced, while in equation (1) the magnesium sulfate, a bi-bivalent salt, has a very much lower ionization than the other salts, and therefore the amount of sulfate ion withdrawn in the form of un-ionized magnesium sulfate is large. For this reason the solubility of the "saturating salt" is much more increased by metathesis number (1) than it is in the remaining three cases.

Nitric acid has a much greater solvent effect upon silver sulfate than either potassium nitrate or magnesium nitrate. This is a result to be expected on account of the formation of the intermediate HSO_4^- ion by the metathesis.

15. Types of Solubility Curves for Bi-bivalent Salts.

Since diionic salts of either the uni-univalent or the bi-bivalent type are more simple in their constitution than triionic salts, it is to be expected that there will be fewer types of solubility curves. There is, in either of these cases, only one kind of common ion which can be added, so the only types of curves are the one for the addition of a common ion, and that for the addition of no common ion. The characteristic forms of the curves of the two types for the bi-bivalent salt calcium sulfate are presented in Fig. 2. These curves are drawn from the data obtained by different investigators, as presented in Tables XII and XIII. The data are not so complete in dilute as they are in concentrated solutions. They will be discussed from a more quantitative standpoint in a later paper.

TABLE XII.—SOLUBILITY OF CALCIUM SULFATE IN AMMONIUM SULFATE SOLUTIONS ACCORDING TO SULLIVAN.[1]

(Concentrations in milliequivalents per liter.)

Concentration $(NH_4)_2SO_4$.	Density of $(NH_4)_2SO_4$.	Solubility $CaSO_4$.	Density of mixture 25°/4°.	Sp. cond. $(NH_4)_2SO_4 \times 10^3$.	Spec. cond. mixture $\times 10^3$.
0.00	...	30.60	0.99911	....	2.214
1.9532	0.99711	30.01	0.99911	0.2822	2.394
3.906	0.99721	29.32	0.99920	0.5475	2.546
15.624	0.99765	26.54	0.99946	2.025	3.602
31.26	0.99832	24.36	0.99995	3.801	5.085
62.50	0.99953	22.62	1.00104	7.083	8.106
125.00	1.00201	21.15	1.00341	13.06	13.88
250.00	1.00681	21.37	1.00817	23.91	24.57
500.00	1.01606	23.75	1.01763	43.32	43.89
1500.0	1.05143	34.22	1.05344	109.0	109.1
3000.0	1.10059	48.91	1.10324	185.3	184.6
6000.0	1.18843	66.10	1.19149	268.8	265.2

[1] THIS JOURNAL, 27, 532 (1905).

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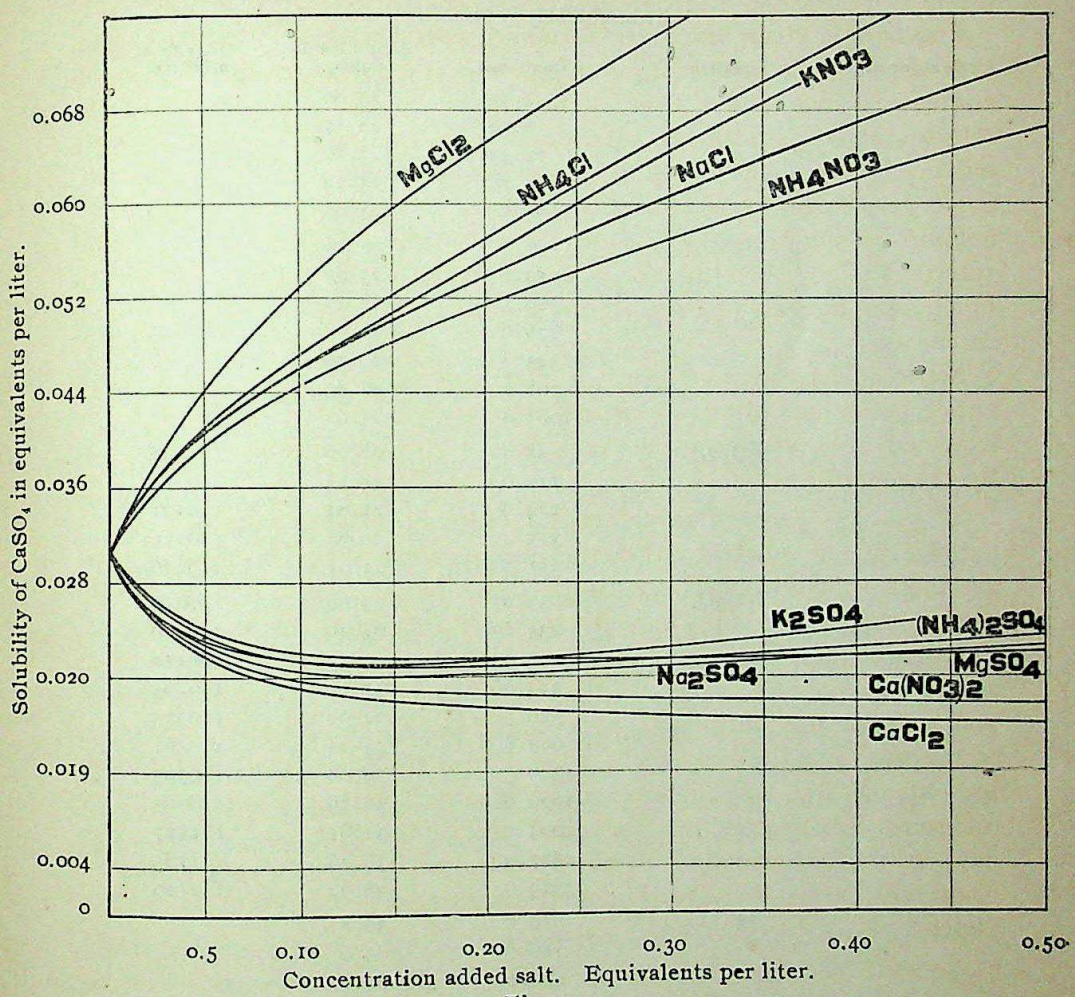

Fig. 2.

TABLE XIII.—SOLUBILITY OF CALCIUM SULFATE IN SOLUTIONS OF SALTS.
(Concentrations in milliequivalents per liter.)

Temperature.	Salt.	Conc. salt.	Solubility of $CaSO_4$.	Density of mixture.
25° C.	$CaCl_2$[1]	0.0	30.42	
		136.0	18.42	
		217.2	17.48	
		468.0	16.22	
		582.0	15.98	
	$Ca(NO_3)_2$[2]	0.0	30.7	0.998
		306.0	18.2	1.014
		612.0	17.6	1.032
	$Ca(OH)_2$[3]	0.0	30.55	

[1] Cameron and Seidell, *J. Physic. Chem.*, 5, 643–55 (1901).
[2] Seidell and Smith, *Ibid.*, 8, 493 (1904).
[3] Cameron and Bell, THIS JOURNAL, 28, 1220 (1906).

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TABLE XIII (*continued*).

Temperature.	Salt.	Conc. salt.	Solubility of $CaSO_4$.	Density of mixture.
		2.21	29.80	
		6.28	28.17	
		12.45	27.22	
		21.75	25.28	
		33.5	24.00	
	$MgSO_4$[1]	0.0	30.04	
		53.2	23.79	
		106.1	22.13	
		176.6	21.60	
		345.8	21.70	
		708.3	22.89	
		1065.0	23.62	
	K_2SO_4[2]	58.42	22.96	1.0038
		113.0	21.24	1.0075
		224.6	21.81	1.0151
		325.4	22.84	1.0229
		351.9	23.31	1.0236
	Na_2SO_4[2]	33.65	23.68	1.0013
		134.23	21.40	1.0076
		198.95	20.39	1.0114
		343.06	21.61	1.0205
		520.7	22.96	1.0315
		649.8	24.24	1.0391
		1326.3	29.08	1.0795
		1620.0	30.79	1.0965
		2064.0	32.81	1.1427
		2887.0	36.76	1.1765
		3619.0	38.92	1.2120
26°	$MgCl_2$[3]	0.0	30.8	
		180.0	63.0	
		406.0	84.2	
		987.6	112.2	
		2570.0	127.6	
		4382.4	97.2	
23	NaCl[4]	0.0	(30.44)	
		17.1	35.2	
		85.2	44.6	
		179.0	52.4	
		520.0	73.6	
		847.1	87.8	
		1301.8	99.8	
		2231.4	111.0	
		33968.0	107.2	

[1] Cameron and Bell, *J. Physic. Chem.*, 10, 212 (1906).
[2] Cameron and Brezeale, *Ibid.*, 8, 337–40 (1904).
[3] Cameron and Seidell, *Ibid.*, 5, 643–55 (1901).
[4] Cameron, *Ibid.*, 5, 560 (1901).

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TABLE XIII (*continued*).

Temperature.	Salt.	Conc. salt.	Solubility of $CaSO_4$.
25	NH_4Cl[1]	201.86	57.28
		456.1	79.02
		873.0	103.85
	NH_4NO_3[1]	124.90	46.71
		312.3	57.73
		687.05	85.19

It has been shown that the curves representing the change of solubility of a unibivalent salt, such as silver sulfate, are not at all of the form to be expected from the solubility-product principle, if the salt added contains the common bivalent ion. However, as the solubility of the dissolved unibivalent salt decreases, the curves of this type rapidly approach what might be considered to be the theoretical curve, although, even in the case of the least soluble salt yet investigated, barium bromate, the actual curve is very far from what would be expected theoretically. The results obtained in this investigation indicate that much less soluble salts would give curves very much nearer the theoretical one; and in order to test this conclusion, the solubilities of the less soluble salts, barium iodate and lead iodate, will be determined. The results are given in the sixth paper of this series. A seventh paper will contain calculations, from the data in this paper, of the ion-concentration product and the un-ionized part of the dissolved salts by the methods outlined in Paper I of this series. It will also contain a discussion of the remarkable abnormalities found in the solubility relations of unibivalent salts.

BOSTON, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 77.]

THE EFFECT OF SALTS UPON THE SOLUBILITY OF OTHER SALTS. VI. THE SOLUBILITY OF DIFFICULTLY SOLUBLE UNIBIVALENT SALTS.

BY WILLIAM D. HARKINS AND W. J. WINNINGHOFF.

Received August 28, 1911.

16. The Solubility of Barium Iodate in Water and in Solutions of Barium Nitrate, Potassium Nitrate and Potassium Iodate.

The results presented in the fifth paper of this series show that, for salts of moderate or of great solubility, there is a very great deviation from the solubility-product principle, when a salt with a common bivalent ion is added to the aqueous solution of a salt in contact with the solid phase and in equilibrium with it. It was observed that the form of the curve representing the change of solubility with the concentration of the added

[1] Cameron and Brown, *J. Physic. Chem.*, 9, 211–13 (1905).

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salt became more nearly what would be expected from this principle as the solubility of the "saturating salt" decreased. It is therefore of interest to determin such solubility curves for salts which are very difficultly soluble.

The salts best suited for such an investigation seemed to be the iodates of barium and lead, whose solubilities in pure water at 25° are 0.001578 and 0.0001101 equivalents per liter, respectively. The molal solubility of lead iodate is only three and one-half times the solubility of silver chloride, and it seems to be the most difficultly soluble unibivalent salt of such a character as to permit of analytical determinations of its concentration of sufficient accuracy. The solubility of this salt was determined in solutions of lead nitrate, potassium nitrate, and in very dilute solutions of potassium iodate. The solubility of barium iodate was determined in solutions of barium nitrate, potassium nitrate, and potassium iodate.

This investigation was carried out with the aid of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

The barium and lead iodates used for the solubility determinations were made by precipitating the respective nitrates with potassium iodate, in a very dilute solution in which the nitrate was kept constantly in excess. The salt was washed with conductivity water until its solubility became constant.

The barium nitrate and potassium nitrate were purified by recrystallization in the same way as was described in the fifth paper of this series. The potassium iodate was recrystallized twice from conductivity water, and the strength of the solutions was determined by analysis.

TABLE I.—THE SOLUBILITY OF BARIUM IODATE IN WATER AT 25°.
(Concentrations in equivalents per liter.)

No.	Solubility.	Mean solubility.	Specific conductance.	Equivalent conductance.	Gram per liter.
1	0.001579		0.00016820	106.5	
2	0.001578		0.00016834		
3	0.001581				
4	0.001581(*s*)				
5	0.001581(*s*)				
6	0.001577(*s*)				
7	0.001575(*s*)	0.001579			0.3845

The concentration of the "saturating salt" was determined by adding potassium iodide to the solution of the iodate, and liberating iodine by adding hydrochloric acid. The iodine was determined by titration with a 0.01 or a 0.005 normal solution of sodium thiosulfate. These dilute thiosulfate solutions were made up as needed by diluting a standard tenth-normal solution. This latter was standardized against iodine, and against a solution of pure copper sulfate. The dilute solutions were constantly checked by titrating against a 0.01 normal potassium iodate

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solution, which was made by weighing out the pure salt which had been dried at 120°. The concentration of this potassium iodate solution was checked by titrating with one of the standard thiosulfate solutions. The thiosulfate solutions were made up with water of a conductivity of about 0.80×10^{-6}, and were kept in a black bottle, which was fitted with soda lime tubes to protect the solution from the action of carbon dioxide. Even the most dilute solutions kept perfectly for a week or more when

TABLE II.—THE SOLUBILITY OF BARIUM IODATE IN SOLUTIONS OF BARIUM NITRATE, POTASSIUM NITRATE AND POTASSIUM IODATE AT 25°.

No.	Added salt.	Conc. added salt.	Solubility $Ba(IO_3)_2$.	Mean sol.	Fractional conc. added salt.	Fractional solubility.
8	$Ba(NO_3)_2$	0.001	0.001361			
9			0.001364(*s*)			
10			0.001363			
11			0.001360(*s*)	0.001362	0.634	0.862
12		0.002	0.001214			
13			0.001213(*s*)			
14			0.001211			
15			0.001211(*s*)	0.001212	1.268	0.768
16		0.005	0.0009740			
17			0.0009757(*s*)			
18			0.0009747			
19			0.0009770(*s*)	0.0009753	3.170	0.619
20		0.020	0.0006739			
21			0.0006752			
22			0.0006749(*s*)			
23			0.0006737(*s*)	0.0006744	12.68	0.427
24		0.050	0.0006128			
25			0.0006133			
26			0.0006137(*s*)			
27			0.0006127(*s*)	0.0006131	31.70	0.388
28		0.100	0.0005663			
29			0.0005655(*s*)	0.0005659	63.4	0.358
30		0.200	0.0005573			
31			0.0005587(*s*)	0.0005580	126.8	0.353
32	KNO_3	0.002	0.001624			
33			0.001625(*s*)	0.001624	1.268	1.029
34		0.010	0.001826			
35			0.001827(*s*)	0.001826	6.34	1.155
36		0.050	0.002640			
37			0.002641(*s*)	0.002640	31.70	1.671
38		0.200	0.003192			
39			0.003189(*s*)	0.003190	126.8	2.021
40	KIO	0.00010608	0.001509			
41			0.001512(*s*)	0.001510	0.0673	0.908
42		0.0005304	0.001240			
43			0.001244(*s*)	0.001242	0.336	0.748
44		0.0010608	0.0009416			
			0.0009421	0.0009418	0.673	0.596

(*s*) after a number denotes that the value was obtained by approaching equilibrium from the side of supersaturation.

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treated in this way. A weight buret was used for all of the titrations. Iodates have a special advantage when it is necessary to make analytical determinations in extremely dilute solutions, since each mol. of barium or lead iodate releases twelve equivalents of iodine from potassium iodide in acid solution.

The results of the solubility determinations, together with the densities of the solutions, are given in Tables I–IV.

17. The Solubility of Lead Iodate in Water and in Solution of Lead Nitrate, Potassium Nitrate and Potassium Iodate.

TABLE III.—SOLUBILITY OF LEAD IODATE IN WATER AT 25°.
(Concentrations in equivalents per liter.)

No.	Solubility of lead iodate.	Mean.	Gram per liter.
46	0.0001105		
47	0.0001102		
48	0.0001107		
49	0.0001101(*s*)		
50	0.0001097(*s*)		
51	0.0001194(*s*)		
52	0.0001097(*s*)	0.0001102	0.0307

TABLE IV.—SOLUBILITY OF LEAD IODATE IN SOLUTIONS OF LEAD NITRATE, POTASSIUM NITRATE AND POTASSIUM IODATE.

No.	Salt added	Conc. added salt.	Solubility $Pb(IO_3)_2$.	Mean solubility.	Fractional conc. salt.	Fractional solubility.
53	$Pb(NO_3)_2$	0.0001	0.0000870			
54			0.0000870(*s*)	0.0000870	0.908	0.790
55		0.001	0.0000408		9.08	0.373
56			0.0000414(*s*)	0.0000411	...	...
57		0.010	0.0000185			
58			0.0000186(*s*)	0.0000185	90.8	0.169
59		0.100	0.000016			
60			0.000016(*s*)	0.000016	908.0	0.145
61		0.500	(0.000030)			
62			(0.000027)(*s*)	(0.000028)	4590.0	(0.259)
63		3.0	(0.00015)			
64			(0.00015)(*s*)	(0.00015)	27240.0	...
65	KNO_3	0.002	0.00011145			
66			0.0001138(*s*)	0.0001141	18.16	1.039
67		0.010	0.0001334			
68			0.0001334(*s*)	0.0001334	90.8	1.211
69		0.050	0.0002037			
70			0.0002037(*s*)	0.0002037	454.0	1.848
71		0.200	0.0002548			
72			0.0002540(*s*)	0.0002544	1816.0	2.311
73	KIO_3	0.00005304	0.0000717			
74			0.0000697	0.0000697		
75			0.0000714(*s*)			
76			0.0000734(*s*)	0.0000715	0.482	0.65
77		0.0001061	0.0000432			
			0.0000442(*s*)	0.0000437	0.963	0.493

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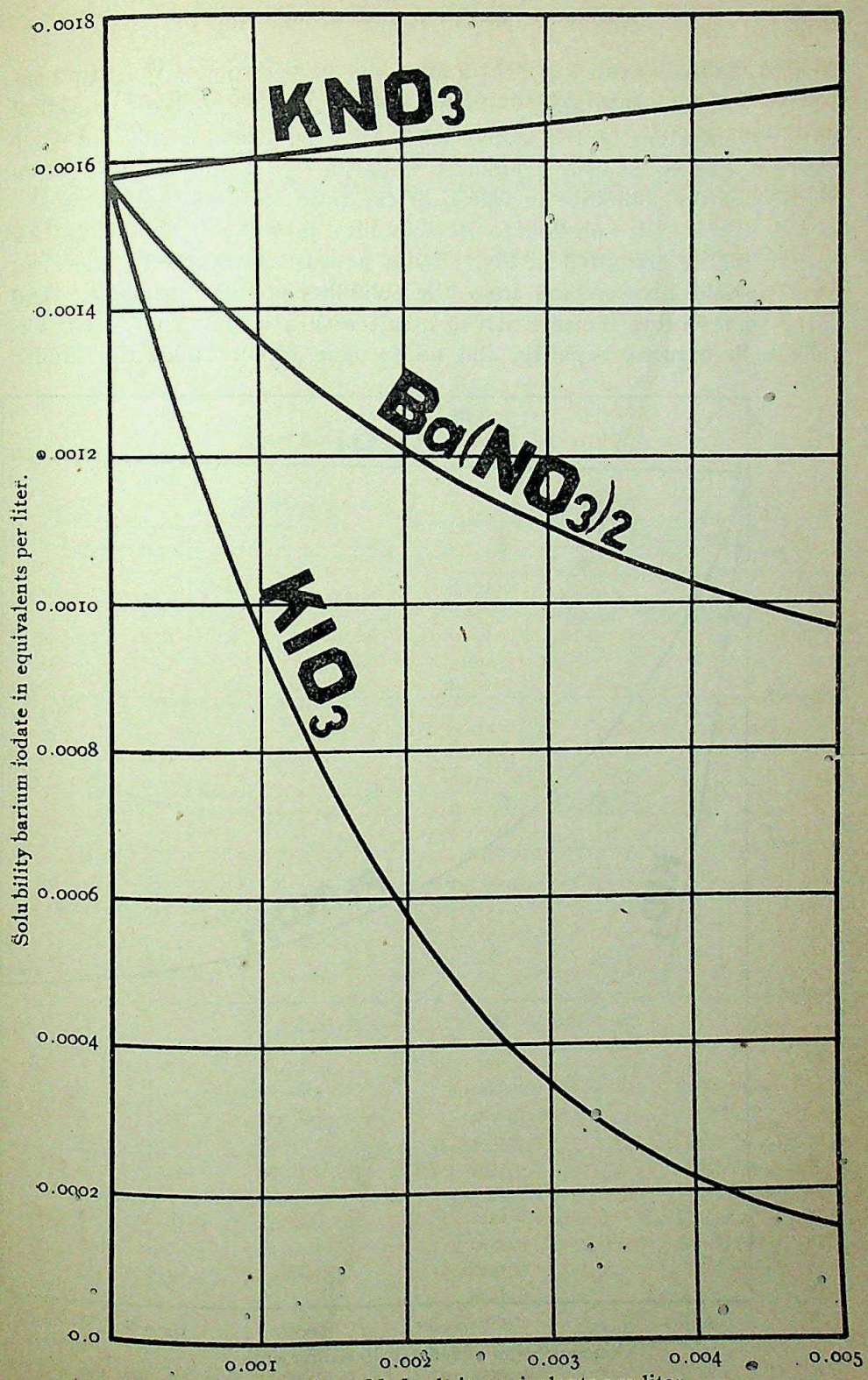

Fig. 1.

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The results of these tables, with other results used for purposes of comparison, are plotted in Figs. 1–3, where the abscissas represent the equivalent concentration of the added salt. In Figs. 1 and 2 the ordinates represent the equivalent solubility, while in Fig. 3 they represent the fraction of the solubility in water, or the ratio of the solubility of dissolved salt in salt solution to its solubility in water. The curves for barium iodate presented in Fig. 1 have, at least qualitatively, the form which would be expected from the solubility-product principle. The curve representing the addition of a salt with a common univalent ion falls with extreme rapidity, and much more rapidly than the similar

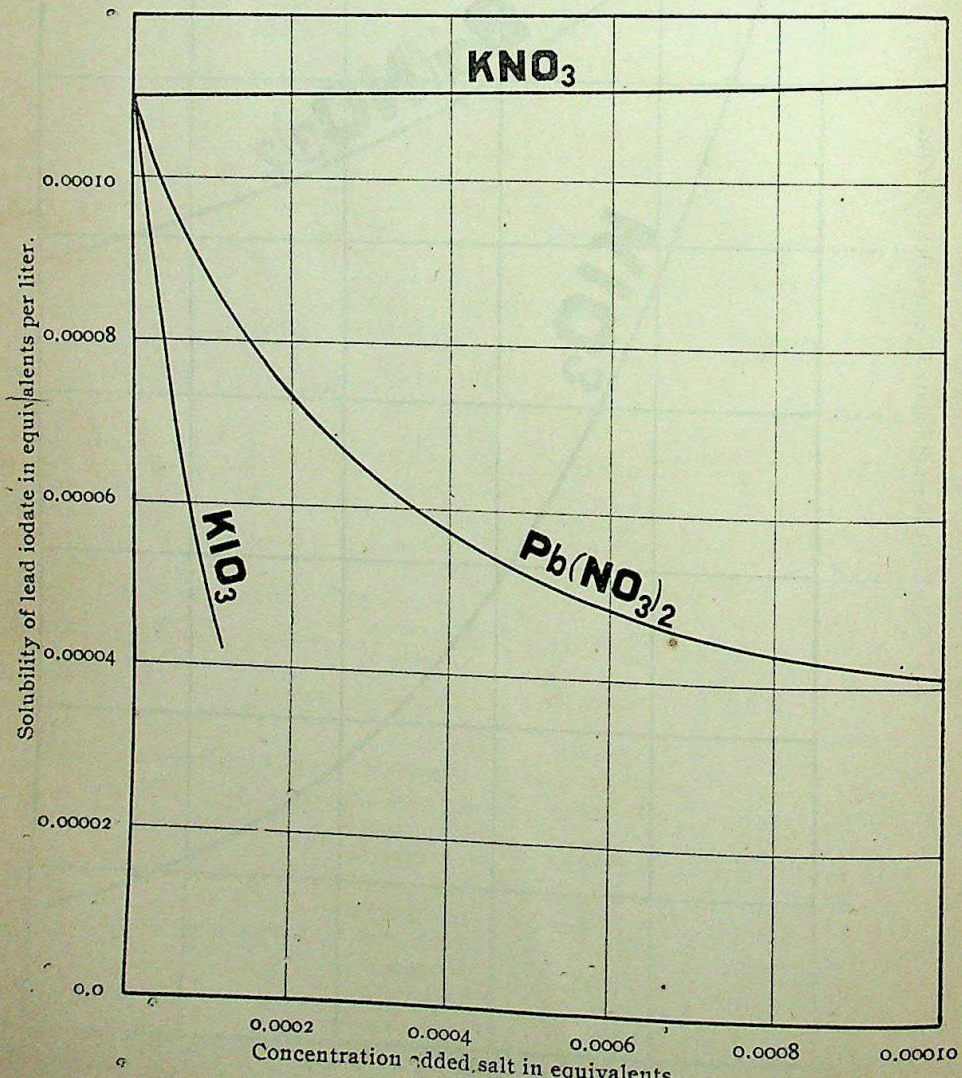

Fig. 2.

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curves for the more soluble salts considered in the fifth paper of this series. The corresponding curve for lead iodate drops very much more rapidly than that for barium iodate.

The curves representing the addition of a salt with a common bivalent ion also drop very rapidly, which is contrary to what was found for the more soluble salts.

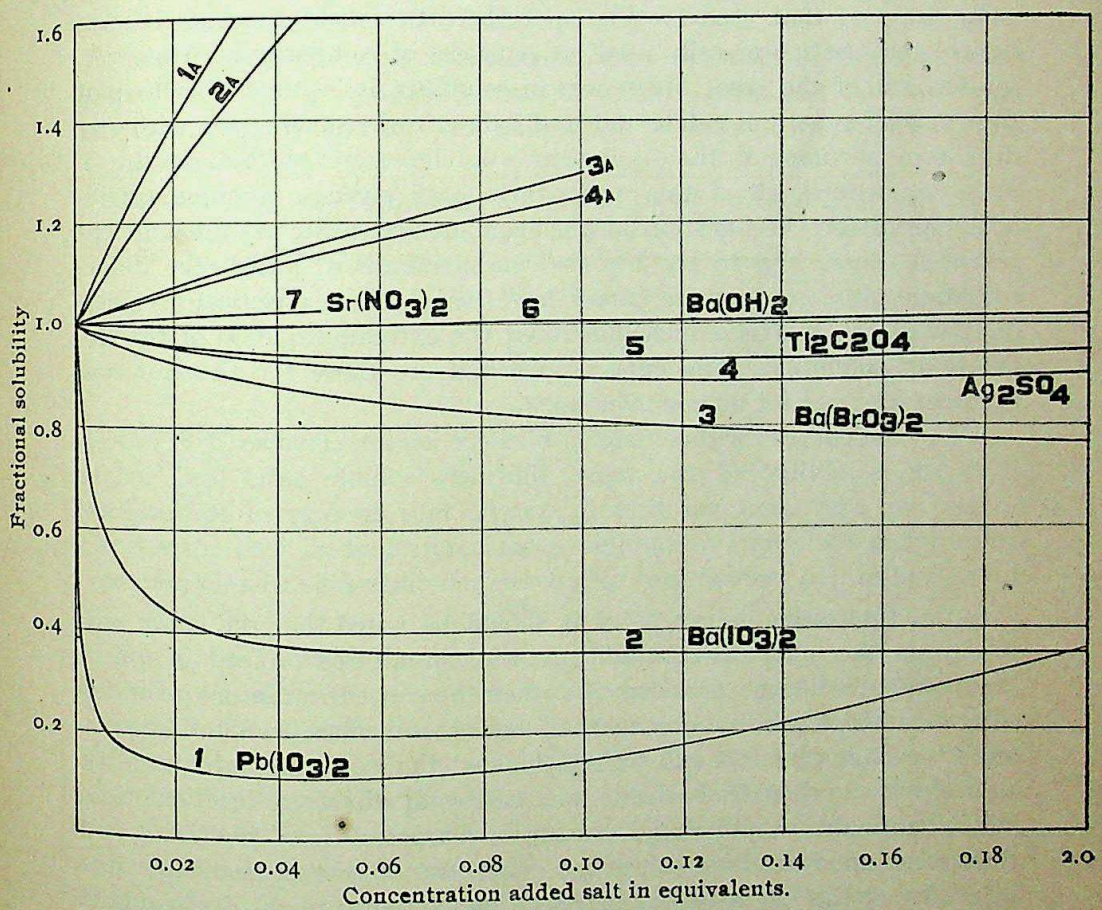

Fig. 3.

No.	"Saturating salt."	Solubility in water.	Added salt.
1	$Pb(IO_3)_2$	0.0001102	$Pb(NO_3)_2$
2	$Ba(IO_3)_2$	0.001579	$Ba(NO_3)_2$
3	$Ba(BrO_3)_2$	0.04018	$Ba(NO_3)_2$
4	Ag_2SO_4	0.05352	K_2SO_4
5	$Tl_2C_2O_4$	0.07536	$K_2C_2O_4$
6	$Ba(OH)_2$	0.562	$Ba(NO_3)_2$
7	$Sr(NO_3)_2$	6.176	$Sr(OH)_2$
1A	$Pb(IO_3)_2$	0.0001102	KNO_3
2A	$Ba(IO_3)_2$	0.001579	KNO_3
3A	$Ba(BrO_3)_2$	0.04018	KNO_3
4A	Ag_2SO_4	0.05352	KNO_3

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The curves for the addition of a salt with no common ion rize very slowly in these figures, but it must be remembered that the concentration of the added salt is given on a very much larger scale than in Fig. 1 of the fifth paper, since the scale is ten times as great for barium iodate, and one hundred times as great for lead iodate.

In Fig. 3 the concentration of the added salt has been plotted on nearly the same scale as that used for Fig. 1 of the fifth article, so that the two figures may be more easily used for purposes of comparison. However, on account of the great differences in solubility it is impossible to plot the curves for barium iodate and lead iodate in the same figure with any degree of accuracy if the equivalent solubilities are plotted on the Y axis, so, instead, all of the curves have been given a common origin. The curves for the addition of the common univalent ion are not represented, since, up to the highest concentrations at which the determinations were made these curves have here become practically coincident with the Y axis, which illustrated the extreme rapidity of the decrease in solubility. The curves presented are those for the common bivalent ion, and for no common ion.

When the curves for the common bivalent ion are considered, it is seen that the solubility of the most difficultly soluble salt, lead iodate (0.0001101 equivalent per liter in water), falls to 0.37 of its original value when the solution contains 0.001 equivalent of lead nitrate per liter,[1] and in 0.01 normal lead nitrate the solubility falls to 16.9 per cent.

As an interesting minor point it should be noted that the curve representing the effect of the addition of lead nitrate to lead iodate in its saturated solutions, turns upward when the concentration of the added salt rizes much above 0.05 normal, and the increase in solubility observed is abnormal. It will be remembered that a similar abnormality was observed when lead nitrate was added to dissolved lead chloride. This abnormality would, then, seem to be characteristic of lead salts, and dependent upon the total salt or ion concentration, rather than upon the solubility of the salt itself. This curve for concentrations of the added salt greater than 0.025 *N* has been drawn as a light line in Fig. 3, since the determinations were not very accurate, on account of the very small

[1] Even this decrease is very small when compared with that caused by a salt containing a common univalent ion, since in the latter case the addition of a salt with a concentration of one-ten-thousandth normal decreases the solubility to 39 per cent. of its original value. If such facts as these were better understood by analysts in general they would add a much smaller excess of the salt used for the precipitations, and thereby reduce the amount of adsorbed salt, and decrease the amount of washing necessary. In this case the addition of so small an amount of potassium iodate as to make the solution 0.00044 normal with respect to this salt, would decrease the solubility of $Pb(IO_3)_2$ to 0.07 of its value in water, and this decrease would be even more rapid for a less soluble salt.

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concentration of the lead iodate present in a solution containing so large an amount of lead nitrate. This latter was precipitated, by the potassium iodide used in the analysis, in the form of lead iodide. This lead iodide oxidizes readily, and the amount oxidized would be added to the concentration of the lead iodate. The determinations in the dilute solutions are not affected by this error.

Table V gives the percentage change in the solubility of the unibivalent salts plotted in Fig. 3, which is caused by making the solution of the salt 0.01 normal with respect to a salt which contains a common bivalent ion or a salt.

TABLE V.—PERCENTAGE CHANGE IN THE SOLUBILITY OF UNIBIVALENT SALTS CAUSED BY MAKING THE SOLUTION 0.01 NORMAL WITH RESPECT TO *A*, A SALT WITH A COMMON BIVALENT ION, *B*, A SALT WITH NO COMMON ION (*viz.*, POTASSIUM NITRATE).

Salt.	Equivalent solubility in water.	Percentage decrease in solubility caused by *A*.	Percentage increase in solubility caused by *B*.
$Pb(IO_3)_2$	0.000110	83.1	21.1
$Ba(BrO_3)_2$	0.001578	48.0	15.5
$Ba(BrO_3)_2$	0.04018	4.3	3.7
Ag_2SO_4	0.05352	3.3	3.3
$Tl_2C_2O_4$	0.07536	2.7	..
$PbCl_2$	0.07776	0.09	..
$Ba(OH)_2$	0.562	0.01	..
$Sr(NO_3)_2$	6.18	—0.08[1]	..

Fig. 3 and Table V deserve careful consideration, as they contain results of great significance. It is unfortunate that no curve has been determined for the solubility of strontium nitrate in a solution of a salt with no common ion, such as potassium chloride; but it may be predicted from the results presented in the figure and the table that this curve will lie practically as low as the curve representing the solubility of strontium nitrate in solutions of strontium hydroxide. In other words, the curves representing the effect of a salt with a common bivalent ion and with no common ion have become practically coincident, at least when the concentration of the added salt is small. This would seem to lead to the interpretation that a 6-normal strontium nitrate solution and a 0.01 normal strontium hydroxide solution have practically no ion in common. The most easily reached explanation of the facts in this case seems to be that presented in the seventh paper of this series, where the assumption is made that very concentrated solutions of a unibivalent salt, using strontium nitrate for an example, consist most largely of the un-ionized salt and the ions $SrNO_3^+$ and NO_3^-, and only an extremely small amount of the Sr^{++} ion, while the solution of strontium hydroxide would consists in this concentrated salt solution, on the basis of the same hypothesis,

[1] That is, 0.08 per cent. increase.

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most largely of $SrOH^-$ and OH^+ ions and un-ionized $Sr(OH)_2$ with only an extremely small amount of the Sr^{++} ion. Under this assumption the ions present, resulting from the dissociation of the two salts, would be almost altogether non-common ions, and the resulting curve should therefore have the same form as for the addition of a salt with no common ion.

BOSTON, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 78.]

THE EFFECTS OF SALTS UPON THE SOLUBILITY OF OTHER SALTS. VII. DISCUSSION OF THE SOLUBILITY RELATIONS OF UNIBIVALENT SALTS.

BY WILLIAM D. HARKINS.

Received August 28, 1911.

18. Introduction.

The data and discussion of the fifth and sixth papers of this series show that the solubility-product principle cannot be even approximately true for moderately soluble salts of the unibivalent type, when a common bivalent ion is added, if the concentration of the un-ionized part remains constant, or varies in the same direction as it always does with uni-univalent salts. In the case of this latter, more simple type of salt the concentration of the un-ionized part of the dissolved salt always decreases with the increase in total ion concentration.[1] If this is true for unibivalent salts, the increase of solubility caused in some cases by the addition of a salt with a common bivalent ion must be accompanied by an enormous increase in the solubility-product. It is therefore of interest to consider these solubility data from a quantitative standpoint, in order to see how much of the variation of the solubility curves from what has been considered the theoretical form may be due to deviations from the solubility-product principle, and how much may be due to irregular behavior on the part of the un-ionized fraction.

With this end in view, calculations of the concentrations of the ionized and un-ionized parts of all of the salts have been made by the methods which have been employed in the study of uni-univalent salts. The method of calculation has been explained in the first paper of this series and illustrated in the fourth paper.[2] It may be recalled that when no common ion is present the total ion concentration (Σi) is taken as the factor determining the ionization relations of the salts. A fundamental assumption made in this method of calculation is that intermediate ions of the type $AgSO_4^-$ or $BaBrO_3^+$ are not present. Indeed, it is

[1] See article IV of this series, THIS JOURNAL, 33, 1683–5 (1911).

[2] See also Sherrill, THIS JOURNAL, 32, 74 (1910).

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TABLE I.—CONCENTRATION OF THE CONSTITUENTS OF SOLUTIONS SATURATED WITH SILVER SULFATE IN MILLIEQUIVALENTS PER LITER.

Salt added.	Conc. salt.	Sol. Ag_2SO_4.	Conc. un-ionized Ag_2SO_4.	Conc. Ag^+.	Conc. $SO_4^=$.	Σi.	Conc. un-ionized KNO_3 or $Mg(NO_3)_2$.	Conc. un-ionized K_2SO_4 or $MgSO_4$.	Conc. un-ionized $AgNO_3$.	Conc. K^+ or Mg^+.	Conc. NO_3^-.	L × 10^3 calc.	L × 10^3 obs.
KNO_3	0.0	53.52	17.02	36.50	36.50	36.50	...	...	...	...	...	...	...
	24.90	57.70	15.41	39.57	37.68	58.67	1.194	4.611	2.725	19.106	20.99	8.434	8.402
	49.75	61.13	14.42	41.86	38.80	79.74	3.956	7.909	4.854	37.88	40.94	11.480	11.410
	99.81	66.93	13.32	45.24	40.72	119.95	12.224	12.881	8.360	74.74	79.23	17.307	17.251
$AgNO_3$	0.0	53.52	17.02	36.50	36.50	36.50	...	...	...	...	...	...	...
	24.96	39.18	13.65	46.84	25.53	46.84	...	...	3.65	...	21.31	6.512	6.497
	49.84	28.45	10.76	59.44	17.69	59.44	...	...	8.09	...	41.75	8.126	8.124
	99.60	16.96	7.27	90.01	9.69	90.01	...	...	19.28	...	80.32	12.136	12.124
K_2SO_4	0.0	53.52	17.02	36.50	36.50	36.50	...	26.532	...	...	...	...	...
	25.015	50.66	18.21	32.45	50.95	50.98	...	14.18	...	18.49	...	7.516	7.490
	50.025	49.35	19.31	30.03	65.90	65.90	...	31.61	...	35.86	...	9.859	9.807
	99.96	48.04	20.94	27.09	95.47	95.47	...	...	...	68.38	...	14.471	14.380
$MgSO_4$	0.0	53.52	17.02	36.50	36.50	36.50	...	...	...	...	...	...	...
	20.014	52.21	17.67	34.54	43.07	43.07	...	11.49	...	8.52	...	6.104	6.122
	50.05	50.93	18.53	32.40	52.70	52.70	...	29.79	...	20.27	...	7.386	7.373
	99.96	49.95	19.73	30.22	68.04	68.04	...	62.14	...	37.82	...	9.437	9.410
$Mg(NO_3)_2$	0.0	53.52	17.02	36.50	36.50	36.50	...	...	...	...	...	...	...
	24.75	59.44	14.89	41.64	33.33	53.77	1.404	11.22	2.909	12.13	20.44	7.416	7.373
	49.57	64.32	13.59	45.37	31.65	71.04	4.824	19.08	5.356	25.67	39.39	9.601	9.526
	99.40	72.69	11.93	51.27	29.98	104.83	15.06	30.79	9.49	53.55	74.85	13.878	13.750

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TABLE II.—CONCENTRATION OF THE CONSTITUENTS OF SOLUTIONS SATURATED WITH BARIUM BROMATE IN MILLIEQUIVALENTS PER LITER.

Salt added.	Conc. salt.	Sol. $Ba(BrO_3)_2$.	Conc. un-ionized $Ba(BrO_3)_2$	Conc. Ba^{++} ions.	Conc. BrO_3^{-} ions.	Σi.	Conc. $KBrO_3$.	Conc. un-ionized $Ba(NO_3)_2$.	Conc. KNO_3.	Conc. K^{+} ions.	Conc. NO_3^{-} ions.	$L \times 10^{3}$ calc.	$L \times 10^{3}$ obs.
KNO_3.....	0.00	40.18	9.68	30.50	30.50	30.50	0.0	0.0	0.0	0.0	0.0	3.660	3.664
	24.99	43.86	8.17	30.99	33.43	52.11	2.258	4.702	1.307	21.41	18.98	6.790	6.784
	50.02	47.03	7.39	31.54	35.68	73.34	3.965	8.101	4.245	41.81	37.66	9.791	9.746
	99.77	52.13	6.56	32.19	38.92	112.59	6.661	13.38	1.271	80.40	73.68	15.458	15.451
$KBrO_3$.....	0.0	40.18	9.68	30.50	30.50	30.50	0.0	...	...	0.0	...	3.660	3.664
	24.97	26.53	7.13	19.40	41.17	41.17	3.20	...	...	21.77	...	5.118	
	49.96	17.37	5.16	12.21	54.94	54.94	7.24	...	...	42.73	...	7.003	6.974
	99.84	8.76	3.02	5.74	88.04	88.04	17.54	...	...	82.30	...	11.357	11.308
$Ba(NO_3)_2$.....	0.00	40.18	9.68	30.50	30.50	30.50	...	0.0	...	...	0.0	3.660	3.664
	24.98	36.47	10.10	44.42	26.37	44.42	...	6.93	...	...	18.05	5.615	5.643
	49.99	34.74	10.54	58.79	24.20	58.79	...	15.40	...	...	34.59	7.599	7.596
	99.92	32.63	11.18	86.05	21.45	68.05	...	35.32	...	...	64.60	11.349	11.325

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upon this assumption that our present values for the ionization of uni-bivalent salts are based.

19. Calculation of the Concentration of the Constituents of Mixtures.

The concentrations of the various constituents in the mixtures calculated in this way are given in Tables I to IV. The concentration of the un-ionized part of the saturating salt is given in the fourth column, the total ion concentrations in the sixth column, and the calculated and observed conductances in the last two columns. The conductance data upon which these calculations are based are given in Tables VIII to IX of the fifth paper of this series. The values of the equivalent conductances for all of the added salts were obtained by interpolation, while those for the dissolved salt were obtained by extrapolation, using the formula $1/\Lambda = 1/\Lambda_0 + K(C\Lambda)^{2-n}$, where the values of K and n were determined from the experimental values of Λ for each salt, and n was so chosen as to give nearly a straight line graph when the values of $1/\Lambda$ are plotted against $(C\Lambda)^n$. On account of the very low solubility of barium iodate it is not possible to determin the conductance accurately enough by

TABLE III.—CONCENTRATION OF THE CONSTITUENTS OF SOLUTIONS SATURATED WITH LEAD CHLORIDE IN MILLIEQUIVALENTS PER LITER.

Salt added.	Conc. salt.	Sol. $PbCl_2$.	Conc. un-ionized $PbCl_2$.	Conc. Pb^{++} ions.	Conc. Cl^- ions.	Σi.	Conc. KCl or $Pb(NO_3)_2$.	Conc. K^+ or NO_3^-.	$L \times 10^3$ calc.	$L \times 10^3$ meas.
KCl.....	0.0	77.76	34.11	43.65	43.65	43.65	0.0	0.0	...	..
	50.0	48.20	24.76	23.44	66.87	66.87	6.57	43.43	...	..
	100.0	34.10	19.88	14.22	99.18	99.18	15.04	84.96	...	..
$Pb(NO_3)_2$	20.0	77.76	34.11	43.65	43.65	43.65	0.0	0.0	6.42	..
	19.980	76.75	36.41	53.56	40.34	53.56	6.76	13.22	7.803	..
	50.003	76.64	39.67	68.44	36.97	68.44	18.53	31.47	9.894	..
	99.49	77.98	44.43	91.85	33.55	91.85	41.19	58.3	13.199	13.124

TABLE IV.—CONCENTRATION OF THE CONSTITUENTS OF SOLUTIONS SATURATED WITH BARIUM IODATE IN MILLIEQUIVALENTS PER LITER.

Salt added.	Conc. salt.	Sol. $Ba(IO_3)_2$.	Conc. un-ionized $Ba(IO_3)_2$.	Conc. Ba^{++} ions.	Conc. IO_3^- ions.	Σi.	Conc. $Ba(NO_3)_2$.	Conc. NO_3^- or K^+ ions.
$Ba(NO_3)_2$	0.0	1.579	0.091	1.488	1.488	1.488	0.0	...
	1.0	1.362	0.092	2.199	1.270	2.199	0.071	0.929
	2.0	1.212	0.094	2.951	1.118	2.951	0.166	1.834
"	5.0	0.9753	0.101	5.318	0.873	5.318	0.550	4.450
	20.0	0.6744	0.118	16.85	0.556	16.85	4.70	16.30
	50.0	0.6131	0.140	37.57	0.472	37.57	12.90	37.10
	100.0	0.5659	0.172	67.99	0.393	67.99	32.40	67.60
	200.0	0.5580	0.206	120.80	0.351	120.80	79.6	120.4
KIO_3..	0.0	1.579	0.091	1.488	1.488	1.488	...	...
	0.5304	1.242	0.072	1.170	1.683	1.683	0.0174	0.513
	1.0608	0.9418	0.059	0.863	1.908	1.908	0.037	1.024

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extrapolation, so the assumption was made that the ionization of barium iodate differs from that of barium nitrate by the same percentage that the ionization of potassium iodate differs from that of potassium nitrate. The values used were those obtained at 18° by Kohlrausch. The values for the ionization of silver lead sulfate were obtained by dividing the equivalent conductance, as obtained by extrapolation, by the equivalent conductance at zero concentration as given by Hunt.[1] When the ionization values thus obtained were plotted against the total ion concentration the curve was almost the same as that obtained experimentally for thallous sulfate, though for the higher ion concentrations the ionization of silver sulfate is slightly larger. The ionization of barium bromate at the higher ion concentrations was calculated entirely from the extrapolated values of the equivalent conductance. A comparison of the ionization curve with that for barium nitrate makes it seem probable that the values of the ionization obtained for barium bromate are slightly too high for the higher concentrations. However, as it is not certain that these values are too high, and since any correction which should be made is so small that it would make no appreciable difference in the calculations, the values obtained by extrapolation have not been changed.

20. The Solubility Product.

The chief interest in the results presented in Tables I to IV centers in the change of the solubility product $(B^+)^2(A^=)$ or $(B^{++})(A^-)^2$ and of the concentration of the un-ionized part B_2A or BA_2 with the total ion concentration (or with the total salt concentration). In this connection

TABLE V.—VALUES OF THE SOLUBILITY PRODUCT FOR SILVER SULFATE IN THE PRESENCE OF OTHER SALTS.

(Σi in milliequivalents, solubility product in millimoles.)

Σi.	KNO_3.	$AgNO_3$.	K_2SO_4.	$MgSO_4$.	$Mg(NO_3)_2$.
36.50	24320	24320	24320	24320	24320
43.07	...	...	...	25700	...
46.84	...	28010	...	...	...
50.98	...	...	26790	...	...
52.70	...	...	...	27700	...
53.77	...	...	...	...	28900
58.67	29480	...	...	...	...
59.44	...	31280	...	...	...
65.90	...	...	29730	...	...
68.04	...	...	...	31100	...
71.04	...	...	...	...	32570
79.74	33930	...	...	...	...
90.01	...	39250	...	...	...
95.47	...	...	35080	...	...
104.83	...	...	...	...	39410
119.95	41600	...	...	...	...

[1] THIS JOURNAL, 33, 801 (1911).

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the change of concentration of the un-ionized part is the more interesting on account of the very great irregularity of its behavior, but the discussion of this subject will be deferred until the values for the solubility product have been presented. These values, with the corresponding total ion concentrations, are given in Tables V to VIII.

TABLE VI.—VALUES OF THE SOLUBILITY PRODUCT FOR BARIUM BROMATE IN THE PRESENCE OF OTHER SALTS.

(Σi in milliequivalents, solubility product in millimoles.)

Σi.	KNO_3.	$KBrO_3$.	$Ba(NO_3)_2$.
30.50	14190	14190	14190
41.17	...	16880	...
44.42	...	...	15430
52.41	17330	...	...
54.94	...	18420	...
58.79	...	...	17210
73.34	20080	...	...
86.05	...	...	19800
88.04	...	22230	...
112.59	24370	...	...

TABLE VII.—VALUES OF THE SOLUBILITY PRODUCT FOR LEAD CHLORIDE IN THE PRESENCE OF OTHER SALTS.

(Σi in milliequivalents, solubility product in millimoles.)

Σi.		KCl.	$Pb(NO_3)_2$.
43.65	4.162 ←	41620	41620
53.56		...	43580
66.87		50000	...
68.44		...	46730
91.85		...	51700
99.18		69880	...

TABLE VIII.—VALUES OF THE SOLUBILITY PRODUCT FOR BARIUM IODATE IN THE PRESENCE OF BARIUM NITRATE.

(Σi in milliequivalents, solubility product in millimoles.)

Σi.	
1.488	1.648
2.199	1.773
2.951	1.846
5.318	2.025
16.85	2.606
37.57	4.185
67.99	5.245
120.80	7.880

The most striking result presented in these tables is that there is no approach to constancy in the values of the solubility product; for example, it increases 71 per cent. when 0.1 normal potassium nitrate is added to silver sulfate. Under the same conditions the solubility product for

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barium bromate increases about 72 per cent., while that for thallous chloride, a uni-univalent salt, increases only 18½ per cent., although the corresponding increase in the total ion concentration is much greater than for either of the unibivalent salts.

Fig. 1 shows the solubility products for lead chloride, silver sulfate, barium bromate, and for thallous chloride plotted as ordinates against

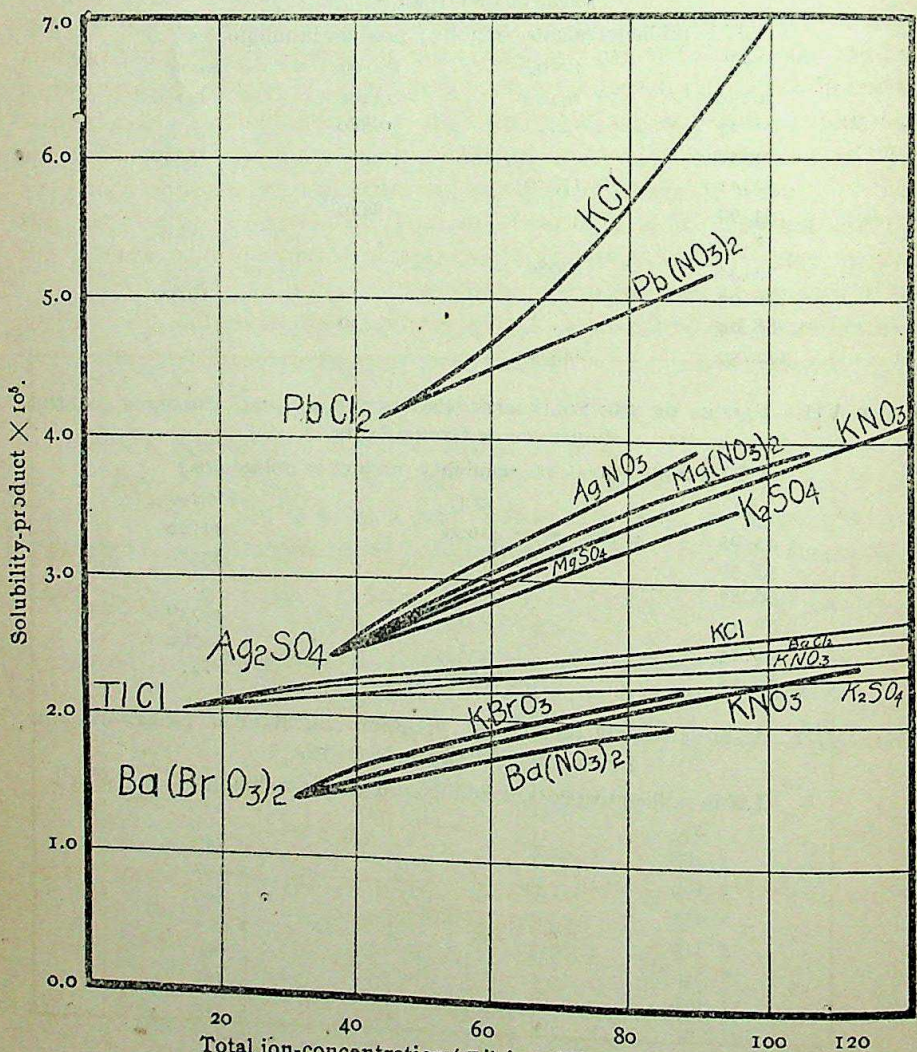

Fig. 1.

the corresponding total ion concentrations as abscissas. It will be seen that the solubility product for the uni-univalent salt thallous chloride increases somewhat, but not very greatly, with an increase in the total

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ion concentration,[1] but that in the case of the unibivalent salts with about the same degree of solubility, the solubility product increases very rapidly with the increase in total ion concentration (Σi) and the increase is much greater for some types of added salts than for others. The increase is greatest when the added salt contains a common univalent ion, and least when it contains a common bivalent ion. Moreover, in the one case in which the comparison is possible, that of silver sulfate, this increase is less rapid when the added salt with the common bivalent ion is a unibivalent salt than when it is a bi-bivalent salt. In the same way, the increase in the solubility product when the added salt contains no common ion is slightly greater when the added salt is unibivalent than when it is uni-univalent. The increase in the solubility product for lead chloride is extremely great when the salt with a common univalent ion is increased in concentration from 0.05 to 0.1 normal. It is of interest to note that lead chloride is the salt which shows the most abnormal increase in total solubility when a salt with a common bivalent ion is added.

In Fig. 2 the logarithms of the solubility product for the various

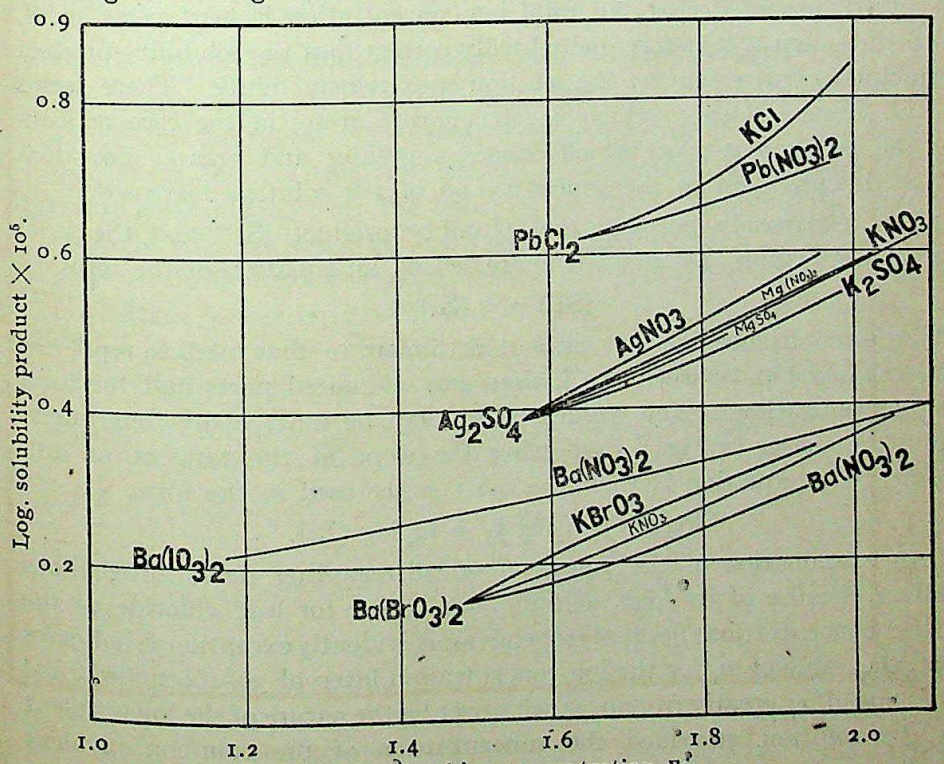

Fig. 2.

[1] This result is typical for uni-univalent salts as shown in the fourth paper of this series.

[2] To get the characteristics for barium iodate subtract 4 on the y axis and 1 on the x axis.

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salts are plotted as ordinates and the logarithms of the corresponding total ion concentration as abscissas. This figure shows more clearly than Fig. 1 the rate of change of the solubility product. Barium iodate is the only salt investigated having a very small solubility (1.578 milliequivalents per liter); and with this salt the rate of increase of the solubility product with the total concentration is very much less than with the more soluble salts, barium bromate (40.18 milliequivalents per liter), silver sulfate (53.52 milliequivalents per liter), and lead chloride (77.76 milliequivalents per liter). This is very marked up to a total ion concentration of 5.3 milliequivalents per liter for solutions of barium iodate. In the more concentrated solutions, with a concentration of added salt between 50 and 100 millinormal (Σi between 37 and 68), the solubility product increases at about the same rate as it does with the more soluble salts at the same ion concentrations. This fact, taken together with the data presented in the sixth paper of this series, shows that the solubility product becomes more constant as the solution becomes more dilute, and that the solubility-product principle is very nearly true for such difficultly soluble salts as lead iodate, even when the common bivalent ion is added, provided that the total ion concentration is kept very small. The statement is therefore undoubtedly correct that the solubility-product principle is true whenever the solution is extremely dilute. There seems to be some influence, which is particularly strong in the case of salts of the unibivalent type, which causes a greater and greater deviation from this principle as the concentration of the solution increases.

The relationship between the solubility product (SP) and the total ion concentration (Σi) may be expressed by an equation of the form

$$(\mathrm{SP}) = k_i(\Sigma i)^{m_i}.$$

This form has been chosen since it is similar to that used to represent the relationship between the ionized and un-ionized parts and the total ion concentration.[1] The values of m_i may be most easily determined from the curves in Fig. 2 by getting the slope of the tangent at any point. The equation is therefore most easily used in the form

$$\log (\mathrm{SP}) = \log k_i + m_i \log (\Sigma i).$$

An examination of the values of m_i, disregarding those for thallous sulfate because of its high solubility and those for lead chloride at the higher concentrations because its behavior is evidently exceptional, indicates that the value of m_i for the ion concentration interval 30–100 millinormal does not differ greatly from 0.45 whatever be the nature of the ions present in the solution, provided the concentration of the common bivalent ion be not increased. When the latter ion is increased in concentration, a somewhat lower value of m_i results, namely about 0.34.

[1] $(A^+)(B^-)/(AB) = K(\Sigma i)^{2-n}$.

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TABLE IX.—VALUES OF m_i AND $\log_{10} k_i$ IN THE EQUATION $\log_{10} [(B^+)^2(A^=)$ OR $(B^{++})(A^-)^2] = \log_{10} k_i + m_i \log_{10} (\Sigma i)$.

Salt B_2A or BA_2.	Added salt.	m_i.	$\log k_i$.	Limits of Σi.	
	Salt with Common Univalent Ion Added.				
Tl_2SO_4[1]	$TlNO_3$	0.88	.....	234.0	312.8
$PbCl_2$	KCl	0.44	+4.340	43.85	66.87
		0.85	+4.000	66.87	99.18
Ag_2SO_4	$AgNO_3$	0.53	+4.085	36.50	90.01
$Ba(BrO_3)_2$	$KBrO_3$	0.43	+4.055	30.50	88.04
	Salt with No Common Ion Added.				
Ag_2SO_4	KNO_3	0.45	+4.134	36.50	119.95
	$Mg(NO_3)_2$	0.45	+4.154	36.50	104.83
$Ba(BrO_3)_2$	KNO_3	0.41	+4.043	30.50	112.59
	Salt with Common Bivalent Ion Added.				
Tl_2SO_4[1]	Na_2SO_4	0.27	+4.043	234.0	334.4
$PbCl_2$	$Pb(NO_3)_2$	0.29	+4.43	43.65	91.85
Ag_2SO_4	K_2SO_4	0.38	+4.170	36.50	95.47
	$MgSO_4$	0.39	+4.165	36.50	68.04
$Ba(BrO_3)_2$	$Ba(NO_3)_2$	0.30	+4.007	30.50	86.05
$Ba(IO_3)_2$	$Ba(NO_3)_2$	0.17	0.187	1.49	5.3

21. The Concentration of the Un-ionized Part.

When salts are added to saturated solutions of non-electrolytes the solubility of the non-electrolyte is, in general, decreased. This is what is known as the "salting out effect." The general magnitude of this effect may be judged from the results upon the solubility of phenylthiocarbamide as determined by Rothmund[2] and by Biltz.[3] They are expressed by Rothmund as the percentage lowering in solubility caused by the addition of one equivalent of the salt to one liter of the solution. In Table X these values divided by 10 are given. They represent approximately the percentage lowering caused by a tenth-normal salt solution.

TABLE X.—PERCENTAGE LOWERING OF THE SOLUBILITY OF PHENYLTHIOCARBAMIDE AT 20°, CAUSED BY THE PRESENCE OF 0.1 NORMAL SALT.

NH_4NO_3	—0.7	KCl	2.4
KI	—0.4	$CuCl_2$	2.5
NaI	0.07	NaCl	2.8
KNO_3	0.8	$(NH_4)_2SO_4$	2.8
$NaNO_3$	1.0	$MgSO_4$	3.2
$KClO_3$	1.22	K_2SO_4	3.7
$NaClO_3$	1.26	Na_2CO_3	3.8
$KC_2H_3O_2$	2.3	Na_2SO_4	4.1

[1] These results for thallous sulfate are derived from the data given in Table X of Paper IV of this series.

[2] Rothmund, *Z. physik. Chem.*, **33**, 401 (1900).

[3] Biltz, *Ibid.*, **43**, 41 (1903).

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The maximum lowering given by Rothmund[1] is about 5.4 per cent., *viz.*, that produced when 0.1 equivalent sodium carbonate or sodium sulfate is added to aqueous solutions of ethyl ether at 18.[2] The percentage lowerings in the solubility of nitrous oxide, oxygen, and carbon dioxide, caused by 0.1 normal sulfuric acid, are 0.87, 1.07 and 0.68, respectively. If the salts are arranged in the order in which they affect the solubility of one non-electrolyte, they are, with few exceptions, arranged in the order in which they influence the solubility of any other slightly soluble non-electrolyte. The constancy of the magnitude of the equivalent lowering of solubility may be judged from the following values obtained by adding magnesium sulfate to solutions of the following substances: Hydrogen, 23; nitrous oxide, 29; carbon dioxide, 30; phenylthiocarbamide, 32; ethyl acetate, 39; and from the following ones obtained when sodium chloride is the added salt: Hydrogen, 21.5; nitrogen, 34; nitrous oxide, 24; oxygen, 27.6; carbon dioxide, 21; hydrogen sulfide, 15; phenylthiocarbamide, 28; ethyl acetate, 34; and ethyl ether, 42. (All of the results for ethyl ether are very high.)

If then, the un-ionized part of a salt in aqueous solution is similar in its properties to a non-electrolyte, it would be expected that the addition of 0.1 normal potassium chloride would cause a decrease in solubility of about 2.4 per cent.; of 0.1 normal potassium sulfate, a decrease of about 3.7 per cent.; and of potassium nitrate, of about 0.8 per cent. The results for the uni-univalent type of salt[3] have shown that the solubility of the un-ionized part of thallous chloride decreases from 17.55 milliequivalents in pure water to 9.7 in tenth-normal potassium nitrate solution, to 9.7 in tenth-normal potassium sulfate solution, and to 10.9 in tenth-normal thallous sulfate solution, that is, by 44.7, 44.7, and 37.9 per cent., respectively. This is more than 10 times the lowering caused by the salting out of non-electrolytes. It seems clear then that the lowering of the solubility of the un-ionized part of an electrolyte caused by the addition of a salt is of a different order of magnitude from the ordinary salting-out effect.[4]

When salts of different types are added in solutions of uni-univalent salts, the concentration of the un-ionized part of the latter has been shown[5] to be decreased by practically the same amount by the same change in

[1] "Loslichkeit und Löslichkeits Beeinflussigung," p. 153.

[2] Euler, *Z. physik. Chem.*, 49, 303 (1904).

[3] See the fourth paper of this series.

[4] This may be considered as an argument in favor of the consideration of the un-ionized part of a salt as a complex, rather than as an individual substance. It is probable that the equilibria involved in the process of solution are more numerous than is usually supposed. Thus it seems probable that the solid phase is itself partly ionized.

[5] Bray, Paper IV of this series, THIS JOURNAL, 33, 1676 (1911).

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total ion concentration (Σi) whether the added salt is uni-univalent or unibivalent, and whether it has a common ion or no common ion. Thus the values of the concentration of the un-ionized part of thallous chloride in different solutions saturated with it, at the corresponding total ion concentrations (Σi) are as follows:

Added salt.	Σi.	Conc. un-ionized TlCl.
None	14	1.755
0.1 N KNO_3	97	0.97
0.1 N K_2SO_4	85	0.97
0.1 N Tl_2SO_4	64	1.09

The results for unibivalent salts are very different, as will be seen from Tables XI to XIV.

TABLE XI.—CONCENTRATION OF THE UN-IONIZED PART OF SILVER SULFATE IN SOLUTIONS OF OTHER SALTS. (CONCENTRATIONS IN MILLIEQUIVALENTS PER LITER.)

Σi.	KNO_3.	$Mg(NO_3)_2$.	$AgNO_3$.	K_2SO_4.	$MgSO_4$.
36.50	17.02	17.02	17.02	17.02	17.02
43.07	...	...	...	...	17.67
46.84	...	...	13.65	...	...
50.98	...	...	...	18.21	...
52.70	...	...	...	...	18.57
53.77	...	14.89	...	...	...
58.67	15.41	...	...	...	...
59.44	...	...	10.76	...	...
65.90	...	...	...	19.31	...
68.04	...	...	...	...	19.73
71.04	...	13.59	...	...	...
79.74	14 42	...	...	...	...
90.01	...	...	7.27	...	...
95.47	...	...	...	20.94	...
104.83	...	11.93	...	...	...
119.95	13.32	...	...	...	...

TABLE XII.—CONCENTRATION OF THE UN-IONIZED PART OF BARIUM BROMATE IN SOLUTIONS OF OTHER SALTS.

Σi.	KNO_3.	$KBrO_3$.	$Ba(NO_3)_2$.
30.50	9.68	9.68	9.68
41.17	....	7.15	...
44.42	....	....	10.09
52.41	8.17	....	...
54.94	....	5.17	...
58.79	....	....	10.55
73.34	7.38	....	...
86.05	....	....	11.15
88.04	....	3.02	...
112.59	6.57	....	...

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TABLE XIII.—CONCENTRATION OF THE UN-IONIZED PART OF LEAD CHLORIDE IN SOLUTIONS OF OTHER SALTS.

Σi.	KCl.	$Pb(NO_3)_2$.
43.65	34.11	34.11
53.56	...	36.41
66.87	24.76	...
68.44	...	39.67
91.85	...	44.43
99.18	19.88	...

TABLE XIV.—CONCENTRATION OF THE UN-IONIZED PART OF BARIUM IODATE IN SOLUTIONS OF OTHER SALTS.

Σi.	$Ba(NO_3)_2$.	KIO_3.
1.488	0.091	0.091
1.683	...	0.072
1.908	...	0.059
2.199	0.092	...
2.951	0.094	...
5.318	0.101	...
16.85	0.118	...
37.57	0.140	...
67.99	0.172	...
120.80	0.206	...

The results presented in Tables XI to XIV are expressed graphically in Fig. 3, where the ordinates represent the logarithm of the "un-ionized concentration" of the "saturating salt," and the abscissas the logarithm of the total ion concentration. These tables and figures show that the un-ionized part is very much more irregular in its behavior than the solubility product (see Figs. 1 and 2), and also very much more irregular than the un-ionized part of a uni-univalent salt. The latter fact is made plain by Fig. 3, where the lines representing the change in concentration of un-ionized thallous chloride lie so close together that they make almost one line, while the curves for the unibivalent salts diverge widely in the shape of a fan.

Certain remarkable regularities are observed when the "saturating salt" is of the unibivalent type:

(1) When a salt with a common bivalent ion is added the concentration of the un-ionized part of the "saturating salt" always increases rapidly, and this is true whether the added salt is unibivalent or bi-bivalent. This is quite contrary to what is known in regard to the solubility of the un-ionized part of uni-univalent salts in dilute solutions. This increase corresponds to the increase in the total solubility of the salt (see Fig. 1, fifth paper of this series, and discussion) when a salt with a common bivalent ion is added.

(2) When a salt with no common ion is added, the solubility of the un-

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ionized part decreases with increasing total ion concentration, and at about the same rate as the un-ionized part of the uni-univalent salt, thallous chloride decreases. The un-ionized part of a uni-univalent salt decreases at a certain rate with the increase in the total ion concentration, and this

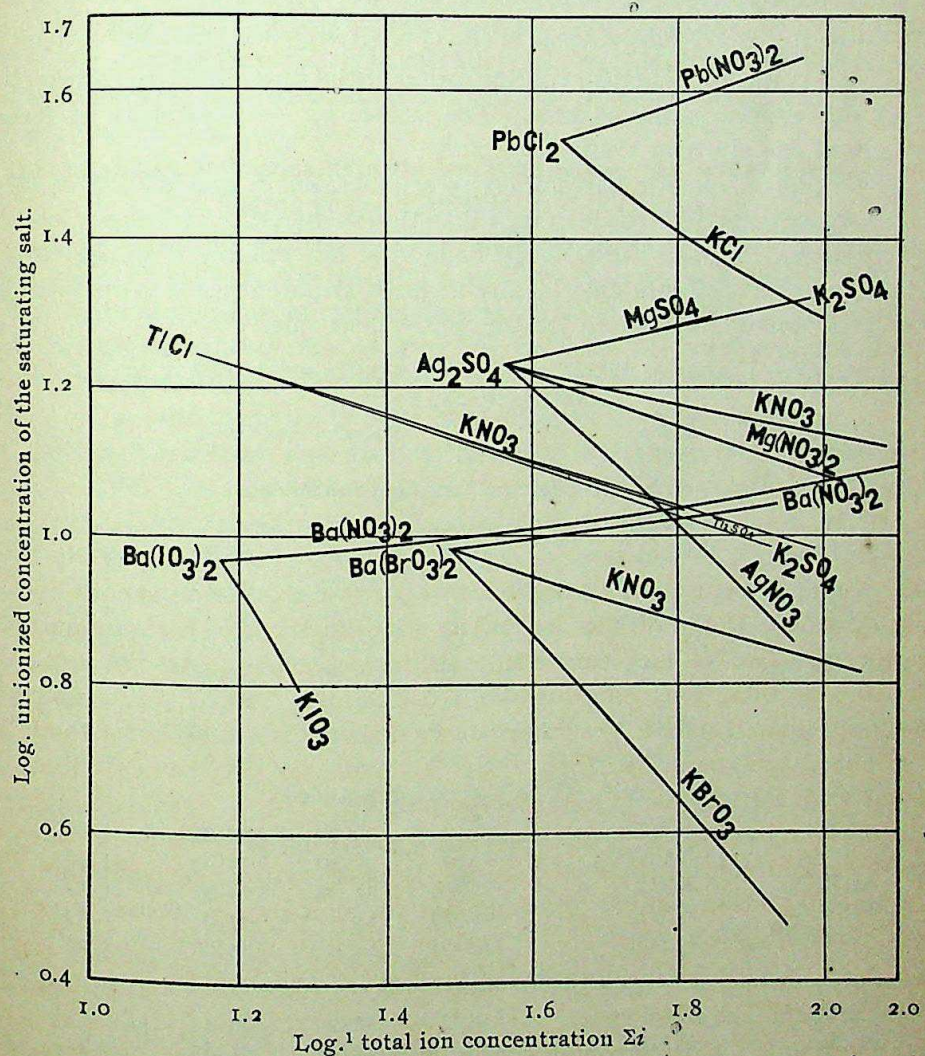

Fig. 3.

rate of decrease is practically the same whether the added salt contains a common ion or not, and whether it is uni-univalent or unibivalent; furthermore, this rate of decrease for the one case investigated is also practically the same as that of the un-ionized unibivalent salt, but only when the salt added to the latter contains no common ion.

(3) When a salt with a common univalent ion is added, the un-ionized

[1] To get the characteristics for barium iodate 2 on the y axis, and 1 on the x axis.

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concentration of the saturating univalent salt decreases with extreme rapidity, and at a rate which is not at all comparable with that for uni-univalent salts.

The results represented by Fig. 3 may also be expressed by equations of the form used for the solubility product, namely,

(B_2A) or $(A_2B) = S_o(\Sigma i)m_u$ or $\log[(B_2A)$ or $(A_2B)] = m_u \log(\Sigma i) + \log S_o$,

where S_o is the hypothetical concentration of the un-ionized part when the total ion concentration is zero. The values of the constants in these equations are given in Table XV.

The values of m_u for barium iodate are inclosed in brackets, since certain assumptions were made in regard to the conductance of barium iodate solutions which make these results somewhat less reliable than the other. The values for thallium chloride are inclosed in parentheses to distinguish its values of m_u from those for the unibivalent salts.

TABLE XV.—VALUES OF m^u, Σi, AND S_o, FOR THE UN-IONIZED PART OF SALTS IN SATURATED SOLUTIONS.

Saturating salt.	Added salt.	m_u.	Minimum Σi.	Maximum Σi.	S_o.
	Salt with Common Univalent Ion Added.				
Tl_2SO_4	$TlNO_3$	—0.62	234.0	312.8	....
$PbCl_2$	KCl	—0.76	43.65	66.87	2.016
			66.87	99.18	1.85
Ag_2SO_4	$AgNO_3$	—0.89	36.50	59.44	1.727
		—1.00	59.44	90.01	1.812
$Ba(BrO_3)_2$	$KBrO_3$	—1.06	30.50	54.94	1.500
		—1.15	54.94	88.04	1.570
$Ba(IO_3)_2$	KIO_3	[—1.70]	1.487	1.907	—1.24
TlCl	Tl_2SO_4	(—0.32)	14.0	64.0	1.29
	Salt with No Common Ion Added.				
Ag_2SO_4	KNO_3	—0.21	36.50	119.95	1.348
	$Mg(NO_3)_2$	—0.37	36.50	104.83	1.420
$Ba(BrO_3)_2$	KNO_3	—0.30	30.50	112.59	1.129
TlCl	KNO_3	(—0.31)	14.0	97.0	1.29
	K_2SO_4	(—0.33)	14.0	85.0	1.29
	Salt with Common Bivalent Ion Added.				
Tl_2SO_4	Na_2SO_4	+0.27	234.0	334.4	...
$PbCl_2$	$Pb(NO_3)_2$	+0.346	43.65	91.85	1.312
Ag_2SO_4	$MgSO_4$	+0.23	36.50	68.04	1.102
	K_2SO_4	+0.215	36.50	95.47	1.110
$Ba(BrO_3)_2$	$Ba(NO_3)_2$	+0.133	30.50	86.05	0.920
$Ba(IO_3)_2$	$Ba(NO_3)_2$	[+0.12]	2.95	16.86	—2.95
$Ba(IO_3)_2$	$Ba(NO_3)_2$	[+0.06]	1.487	2.950	—2.92

These values of m_u indicate that the increase in the un-ionized concentration, when a salt with a common bivalent ion is added, becomes more normal as the solution becomes more dilute, while the decrease in that

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concentration produced by the addition of a salt with a common univalent ion seems to become more abnormal as the concentration of the solution decreases.

The change in the calculated values of the concentration of the un-ionized substance, as exhibited by Table XI, is so enormous, and the influence upon them of the various types of ions, as shown by Table XII, is so extraordinarily different, that it raises serious doubt as to whether they really represent that concentration at all—whether, in other words, they are not so affected by some deviation or superposed effect as to make them of little significance.

22. Solubility Relations Shown by Expressing the Concentrations in Terms of the Solubility in Pure Water.

Instead of carrying these calculations further at this point, it has seemed advizable to examin the existing solubility data by a different method. This method consists in making the equivalent solubility in pure water of the salt saturating the solution the unit for the measurement of all other concentrations. For the purpose of comparison, data on the solubility of uni-univalent salts have been included in this treatment.

Certain additional data taken from the literature are presented in Table XVI. In this table the column headed "Fractional conc. salt" gives the values of the ratio of the equivalent concentration of the added salt to the equivalent solubility of the saturating salt in pure water, while the column headed "Fractional solubility" gives the values of the ratio of the solubility of the salt in the salt solution to the solubility of the salt in water. All concentrations are expressed in milliequivalents per liter.

TABLE XVI.—VALUES OF THE FRACTIONAL SOLUBILITY.

Added salt.	Conc. of added salt.	Solubility.	Fractional conc. of salt added.	Fractional solubility.	Density of solution.
Solubility of Calcium Hydroxide at 20°.[1]					
$Ca(OH)_2$	0.0	41.72	0.0	1.000	
	10.0	33.5	0.240	0.804	
	40.0	20.3	0.959	0.487	
	66.6	13.9	1.595	0.333	
	125.0	6.4	3.000	0.154	
	200.0	3.9	4.795	0.094	
	500.0	0.7	...	...	
Solubility of Strontium Chloride at 0°.[2]					
HCl	0.0	5160.0	0.0	1.00	1.334
	610.0	4480.0	0.1182	0.868	1.304
	1275.0	3785.0	0.2471	0.734	1.269
	2330.0	2720.0	0.4517	0.527	1.220
	2838.0	2200.0	0.5499	0.426	1.201

[1] d'Anselme, *Bull. soc. chim.*, [3] 29, 938 (1903).
[2] Engel, *Ann. chim. phys.*, [6] 13, 376 (1888).

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TABLE XVI (*continued*).

Added salt.	Conc. of added salt.	Solubility.	Fractional conc. of salt added.	Fractional solubility.	Density of solution.
	3725.0	1400.0	0.7220	0.271	1.167
	5275.0	6425.0	1.022	0.0824	1.133
Solubility of Sodium Chloride in Solutions of Hydrochloric Acid at 30°.[1]					
HCl.....	0.0	5400.0	0.0	1.00	1.2018
	457.5	4932.0	0.0488	0.914	1.1906
	969.0	4386.0	0.1794	0.812	1.1801
	1786.0	3589.0	0.3310	0.664	1.1633
	2412.0	2978.0	0.4466	0.552	1.1512
	3052.0	2463.0	0.5656	0.456	1.1427
	4152.0	1628.0	0.7692	0.301	1.1289
	5950.0	630.0	1.102	0.1167	1.1188
	7205.0	268.0	1.335	0.0496	1.1258
Solubility of Silver Propionate at 18.2°.[2]					
Sodium propionate...	0.0	46.2	0.0	1.0	
	16.7	39.3	0.3615	0.851	
	33.3	34.5	0.721	0.747	
	66.7	25.8	1.444	0.5585	
	133.3	19.1	2.886	0.4137	
	266.7	13.1	5.71	0.2828	
	500.0	10.1	10.82	0.2188	
Solubility of Silver Butyrate at 18.2°.[2]					
Sodium butyrate....	0.0	22.4	0.0	1.0	
	6.6	19.9	0.2948	0.889	
	16.4	16.9	0.732	0.755	
	32.9	13.1	1.469	0.585	
	65.8	9.1	2.94	0.4062	
	131.5	6.0	5.875	0.2679	
	263.0	4.0	11.74	0.1785	
	493.0	2.7	22.01	0.1205	
Solubility of Silver Chloroacetate at 16.9°.[2]					
Sodium chloroacetate.	0.0	64.4	0.0	1.0	
	33.3	49.9	0.517	0.775	
	66.7	40.5	1.035	0.6295	
	133.3	29.9	2.07	0.4642	
	266.7	20.8	4.14	0.323	
	500.0	16.2	7.77	0.2518	
Solubility of Silver Acetate at 16°.[2]					
$AgNO_3$.....	0.0	60.3	0.0	1.0	
	6.1	41.7	1.011	0.6916	
	11.9	34.1	1.974	0.5656	
	23.0	19.5	3.814	0.3234	
$NaC_2H_3O_2$.....	0.0	59.3	0.0	1.00	
	33.3	47.4	0.562	0.798	

[1] Masson, *J. Chem. Soc.*, 99, 1132 (1911).

[2] Arrhenius, *Z. physik. Chem.*, 11, 396 (1893). For concentration of the un-ionized part see Stieglitz, THIS JOURNAL, 29, 1538 (1908).

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TABLE XVI (*continued*).

Added salt.	Conc. of added salt.	Solubility.	Fractional conc. of added salt.	Fractional solubility.	Density of solution
	66.7	38.4	1.125	0.648	
	133.3	28.2	2.248	0.476	
	266.7	20.3	4.495	0.342	
	500.0	14.7	8.43	0.248	
Solubility of Silver Valerate.[1]					
Na valerate.....	0.0	9.5	0.0	1.0	
	17.5	4.7	1.84	4.95	
	34.9	3.0	3.67	3.16	
	68.9	1.8	..	..	
	139.5	1.5	..	..	
Solubility of Silver Bromate at 25°.[2]					
$AgNO_3$.....	0.0	8.10	0.0	1.0	
	8.50	5.10	1.049	0.63	
	34.60	2.16	4.272	0.267	
Mean Solubility of TlCl in Solutions of KCl, NH_4Cl and NaCl at 25°.[2]					
KCl, NH_4Cl or NaCl.	0.0	16.12	0.0	1.0	
	25.0	8.72	1.551	0.541	
	50.0	5.92	3.102	0.367	
	100.0	3.97	6.2	0.246	
	200.0	2.69	..	..	
	800.0	1.70	..	..	
Solubility of Thallium Chloride at 25°.[2]					
$TlNO_3$.....	0.0	16.12	0.0	1.0	
	25.0	8.83	1.551	0.548	
	50.0	6.26	3.102	0.388	
	100.0	4.28	6.2	0.265	
Tl_2SO_4.....	0.0	16.07	0.0	1.0	
	19.99	10.34	1.243	0.643	
	49.99	6.772	3.111	0.421	
	99.97	4.679	6.22	0.291	
Solubility of Potassium Perchlorate at 25°.[3]					
KCl.....	0.0	148.1	0.0	1.0	
	49.73	128.2	0.336	0.865	
	99.33	112.3	0.670	0.758	
K_2SO_4.....	0.0	148.1	0.0	1.0	
	49.70	131.5	0.336	0.887	
	99.22	118.1	0.670	0.797	
Solubility of Barium Hydroxide.[4]					
$Ba(NO_3)_2$.....	0.0	561.9	0.0	1.0	
	33.2	561.5	0.0581	0.999	
	111.3	568.5	0.198	1.011	

[1] Arrhenius, *Loc. cit.*

[2] Noyes, *Z. physik. Chem.*, 9, 629 (1892).

[3] Boggs, second article of this series, THIS JOURNAL, 33, 1652 (1911).

[4] Parsons and Carson, THIS JOURNAL, 32, 1383 (1910). Parsons and Perkins, *Ibid.*, 32, 1387.

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TABLE XVI (*continued*).

Added salt.	Conc. of added salt.	Solubility.	Fractional conc. of salt added.	Fractional solubility.	Density of solution.
	143.8	567.5	0.256	1.009	
	232.2	580.5	0.414	1.032	
	338.2	587.5	0.602	1.045	
	462.2	601.5	0.833	1.069	
	533.5	611.5	0.950	1.088	
	657.0	624.5	1.170	1.111	
	769.5	632.2	1.370	1.125	
	Solubility of Strontium Nitrate.[1]				
$Sr(OH)_2$	0.0	6176.0	0.0	1.0	
	60.6	6220.0	0.00982	1.008	
	123.5	6270.0	0.0200	1.016	
	279.0	6290.0	0.0454	1.019	
	Solubility of Barium Nitrate.[1]				
$Ba(OH)_2$	0.0	772.0	0.0	1.0	
	198.7	802.0	0.257	1.038	
	412.8	830.0	0.534	1.074	
	645.4	866.0	0.836	1.121	
	Solubility of Thallium Sulfate.[2]				
Na_2SO_4	0.0	216.8	0.0	1.0	
	99.4	216.0	0.459	0.996	
	397.6	234.6	1.834	1.082	
$NaHSO_4$	0.0	216.8	0.0	1.0	
	202.0	232.2	0.932	1.072	
H_2SO_4	0.0	216.8	0.0	1.0	
	98.8	234.4	0.456	1.081	
	197.4	249.8	0.910	1.152	
$Tl(NO_3)_2$	0.0	216.8	0.0	1.0	
	99.6	167.3	0.460	0.772	

The results of Table XVI, together with those presented in Papers V and VI of this series, are reproduced graphically in Fig. 4. The ordinates represent the "fractional solubility" of the dissolved salt, and the abscissas the "fractional concentration" of the added salt.

It will be seen that these curves, all of which represent the change of solubility caused by the addition of a salt with a common ion, fall into three groups, as follows:

I. The lowest group of curves showing the change of solubility of a uni-bivalent salt when the univalent common ion is added.

II. The middle group showing the effect of the addition of a salt with a common ion to a uni-univalent salt.

III. The highest group showing the effect of the addition of the common bivalent ion to a solution of a unibivalent salt.

[1] Parsons and Carson, THIS JOURNAL, 32, 1383 (1910). Parsons and Perkins, *Ibid.*, 32, 1387.

[2] M. A. Stewart, paper II of this series, THIS JOURNAL, 33, 1661 (1911).

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The curves of Groups I and II lie close together, but those of Group III spread apart, forming a fan-shaped bundle. In each group the curves arrange themselves in general in the order of the solubilities of the salts in water, so that the greater the solubility the higher the curve. Exceptions in the case of very soluble salts will be considered later. Exceptions to this rule also occur in cases where the ionizations of the added salts are very different. Thus it will be seen that the curve for any given salt rizes to a higher position when the added salt is changed from one of a greater to one of a smaller ionization.

As the solubility of the salt decreases, the curves of any one group approach a lower limiting position, namely, that occupied by the theoretical curve for a salt of infinitesimal solubility or for a salt whose ionization is complete. The coördinates for these "theoretical limiting curves," designated T. L. C. in the figure, for the three groups were calculated by the following equations:

I. Unibivalent salt with univalent common ion added: $S(S + C)^2 = 1$.

II. Uni-univalent salt with univalent common ion added: $S(S + C) = 1$.

III. Unibivalent salt with bivalent common ion added: $S^2(S + C) = 1$.

With the aid of the plot given in Fig. 4, the solubility in any dilute salt solution of any uni-univalent or unibivalent salt of moderate or slight solubility may be calculated with a fair degree of accuracy by taking into account its solubility in water and the valence types to which it and the added salt belong. As a secondary factor the degrees of ionization of both salts may be considered. The least accurate results will be obtained, in general, when the added salt contains a common bivalent ion. In this case the degree of ionization of the saturating salt must be taken into account. The writer calculated in this way the solubility of silver sulfate in 0.1 normal potassium sulfate, using principally the curves for barium bromate and thallous oxalate, and obtained the value 47.64 milliequivalents per liter while the true value is 48.04. It would have been possible, by a different choice of the corrections, to have found a value as low as 46.57. Even in this latter case the difference between the true and the calculated values is only 1.47 milliequivalents per liter, while the difference between the solubilities in water as determined by Drucker, and by the writer, amounts to 2.12 milliequivalents. Of course it cannot be expected that accurate results will be obtained in regions on the plot where the experimental values already obtained are scanty or inaccurate. Moreover, where the salt is so abnormal in all its solubility and ionization relations as lead chloride, such calculations will be much less accurate.

It is remarkable that the curves of Groups I and II lie so close to the curve for complete ionization (which has been called above the "theoretical limiting curve"). The curves of Group III, on the other hand,

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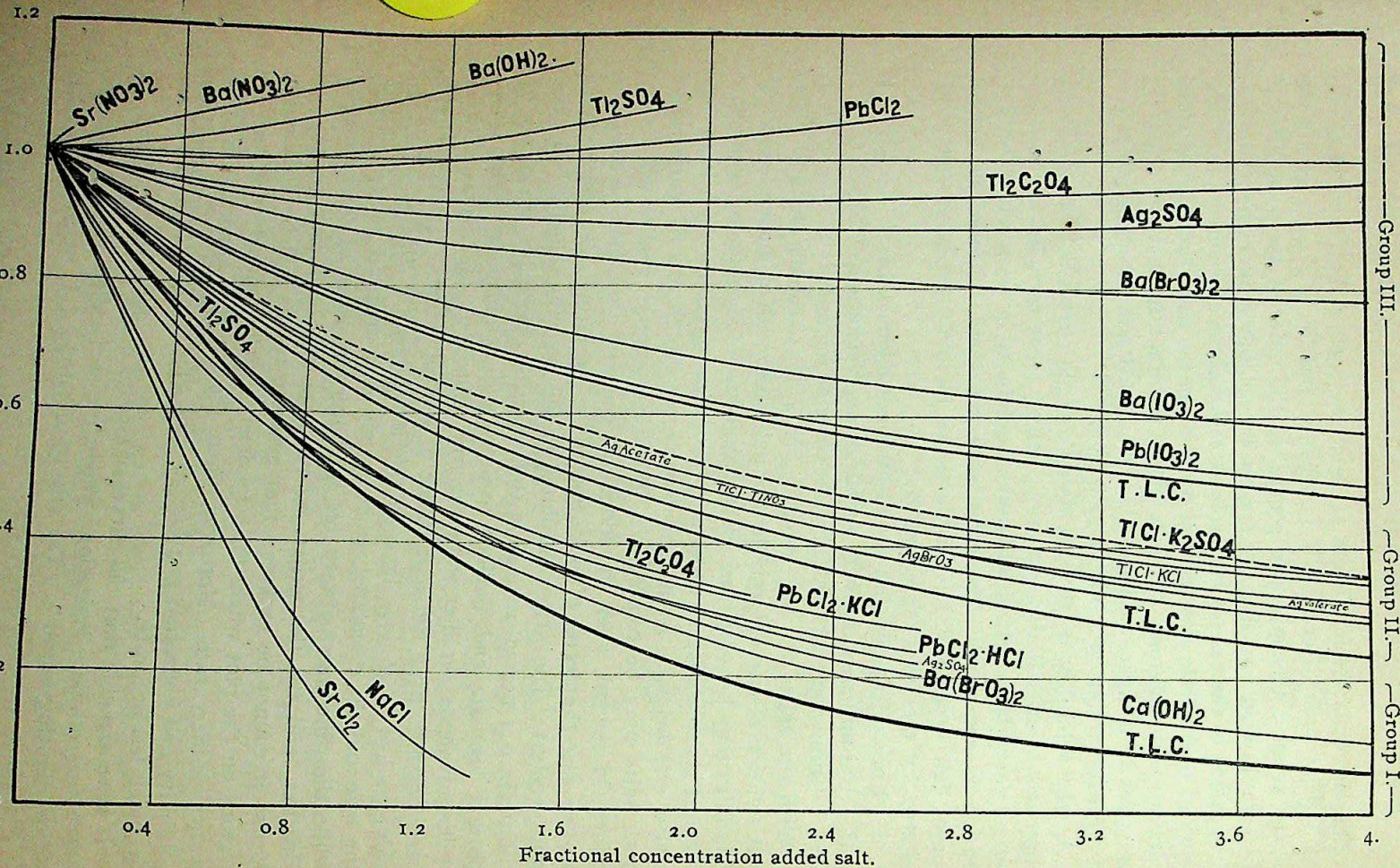

Fig. 4.

"The curve marked $TlCl.K_2SO_4$ in the figure should have been marked $TlCl.Tl_2SO_4$."

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Group I.

No.	Saturating salt.	Solubility.	Added salt.
1.	$Ca(OH)_2$	0.04172	NaOH
2.	$Ba(BrO_3)_2$	0.04018	$KBrO_3$
3.	Ag_2SO_4	0.05352	$AgNO_3$
4.	$PbCl_2$	0.07776	KCl
5.	$PbCl_2$	0.07776	KCl
6.	$Tl_2C_2O_4$	0.07536	$TlNO_3$
7.	Tl_2SO_4	0.2166	$TlNO_3$
*8.	$SrCl_2$	5.16	HCl

Group II.

1.	$AgBrO_3$	0.00810	$AgNO_3$
2.	Ag valerate	0.00950	Na valerate
3.	TlCl	0.01612	KCl
5.	TlCl	0.01612	$TlNO_3$
6.	Ag butyrate	0.0224	Na butyrate
7.	Ag propionate	0.0462	Na propionate
8.[2]	$KClO_4$	0.1481	KCl
9.	Ag acetate	0.0603	Na acetate
10.	TlCl	0.01612	Tl_2SO_4
*11.	NaCl	5.40	HCl

Group III.

1.	$Pb(IO_3)_2$	0.0001102	$Pb(NO_3)_2$
2.	$Ba(IO_3)_2$	0.001579	$Ba(NO_3)_2$
3.	$Ba(BrO_3)_2$	0.04018	$Ba(NO_3)_2$
4.	Ag_2SO_4	0.05352	K_2SO_4
5.	$Tl_2C_2O_4$	0.07536	$K_2C_2O_4$
6.	$PbCl_2$	0.07776	$Pb(NO_3)_2$
7.	Tl_2SO_4	0.2168	Na_2SO_4
8.	$Ba(OH)_2$	0.562	$Ba(NO_3)_2$
9.	$Ba(NO_3)_2$	0.772	$Ba(OH)_2$
10.	$Sr(NO_3)_2$	6.176	$Sr(OH)_2$

The preceding table serves to show that the added salt was in the case of each of the curves represented in Fig. 4, and also to indicate the magnitude of the absolute solubility of each of the saturating salts. The arrangement of the substances in the table (except in the two cases of the very readily soluble salts, sodium chloride and strontium chloride, distinguished by an asterisk) has been made to correspond to the relative positions of the curves on the diagram. How nearly this order corresponds with that of the solubilities of the salts will be readily seen from the column of the table headed "solubility."

[1] The curves for all of the cases listed were drawn in the original drawing, but on account of the reduction of the size of the drawing in the cut, some of the curves for Class 2 have been omitted, but their position is indicated by the order in which the salts are here tabulated.

[2] Only one point has been determined for $KClO_4$, and this lies slightly below the curve for silver acetate though the latter has the smaller solubility; this may be due either to an error in the determination of the solubility of the $KClO_4$, or to the same cause which so greatly lowers the NaCl curve.

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deviate widely from the theoretical curve and from each other. Thus, the solubility of the easily soluble salts strontium nitrate and barium nitrate increases from the beginning with increasing concentration of the added salt when this contains a common bivalent ion. *The curves for these substances have therefore the general form of the curves representing the effect of adding a salt with no common ion.* The solubility of the less soluble salts, thallous sulfate and lead chloride, decreases with the first addition of a salt with a common bivalent ion, but increases on further additions.

The least soluble salt which had been investigated when Fig. 3 was first drawn was barium bromate. The curve for this salt falls considerably at first and then continues to fall slowly up to a concentration of 0.2 normal for the added salt. It has therefore the general form of the theoretical limiting curve, but it still lies very far above it. It was predicted that the curve for barium iodate would lie about two-thirds closer to the theoretical limiting curve, and that the curve for lead iodate would approach much closer still, and this was found to be true when the solubilities of these salts were determined.

Fig. 3 shows that the solubility of unibivalent salts of moderate or slight solubility is decreased to about 50 per cent. by the addition of an equivalent amount of a salt with a common univalent ion. When the saturating salt is uni-univalent the solubility is decreased to about 65 per cent. of that in water, and when a salt with a common bivalent ion is added to a saturated unibivalent salt solution the maximum decrease to be expected is to 75.4 per cent. of the original value.

It will be noted that certain of the experimental curves, all belonging to Group I, fall below the theoretical limiting curves for small additions of the common univalent ion. This is true of the curves for lead chloride in the presence of hydrochloric acid and potassium chloride, and that for calcium hydroxide in the presence of sodium hydroxide. The cause of this phenomenon will be discussed below, in Section 24.

23. The Solubility of Extremely Soluble Salts in Salt Solutions.

It is not the purpose of this paper to consider fully the solubility of very soluble salts, since the writer is now preparing a separate paper on this subject, and since the data are not at present in such shape as to make it safe to generalize. It is, however, worth while at this point to note the fact clearly brought out by the experiments of Engel[1] and Masson[2] that the solubility of many very soluble salts is reduced with great rapidity by the addition of acids and of salts which contain a common ion. Engel explains this great decrease in solubility by assuming that the water is partitioned between the salts. It does not seem to have been recognized, however, that the solubility relations in these con-

[1] *Ann. chim. phys.*, [6] 13, 376 (1888).

[2] *J. Chem. Soc.*, 99, 1132 (1911).

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centrated solutions may be classified according to the types of the saturating and added salts. For salts with a solubility of about one equivalent per liter, the classification into the three groups seems to persist, though the curves for Groups I and II fall below the theoretical limiting curves. Where the solubility is much higher, it becomes impossible to distinguish between the curves of Groups I and II, which fall with extreme rapidity. When a salt with a common bivalent ion is added, the solubility curves (Group III) for every case yet investigated rize as the concentration of the added salt increases.[1] It is quite possible, however, that a decrease could be found in solutions where the added salt has a sufficiently high concentration, since, even when a salt with no common ion is added, there seems to be a tendency for the solubility to decrease under such conditions.

The curves for one very soluble salt for each of Groups I and II have been included in Fig. 4 for the purpose of comparison. It is evident that if we begin with very difficultly soluble salts, the curves rize farther and farther above the theoretical limiting curves as the solubility of the salt increases, until that solubility attains a fairly high value, but then as the solubility increases still further the change in solubility becomes negative, and the curves fall, even very far below the position of the theoretical limiting curve.

24. Theoretical Explanation of the Irregular Solubility Relations of Unibivalent Salts by the Intermediate Ion Hypothesis.

The calculations of this paper have shown that there are certain fairly definit regularities governing the solubility product of unibivalent salts, but scarcely any relating to the concentration of the unionized part. It has, moreover, been seen that these salts exhibit great deviations not only from the theoretical requirements, but also from the more regular behavior of uni-univalent salts. These deviations are, however, so consistent among themselves that it seems evident that they are due to some common cause.

One especially significant fact is that when a salt with a common bivalent ion is added to a very soluble salt of the unibivalent type, the curve has the same form as that representing the effect of the addition of a salt with no common ion. Therefore, the theoretical explanation required would seem to be one which would account for this change from the theoretical form of the curve for difficultly soluble salts in very dilute solutions to this entirely different form in the concentrated solutions. The most obvious assumption is that, as the concentration of

[1] Etard (*Ann. chim. phys.*, [7] 2, 540 (1894)) gave what is possibly an exception to this rule. He finds that the solubility of barium bromide is greatly reduced, and that of barium iodide slightly reduced, each by the presence of the other salt in the solution.

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the solution increases, there is some chemical reaction taking place by which a considerable amount of some new substance is formed by combination of the ions present in the solution.

While the un-ionized concentration of a uni-univalent salt in saturated solution decreases at about the same rate with the increase in total ion concentration whatever be the type of the added salt, the case is very different when the saturating salt is unibivalent. In the latter case the addition of a salt with a common univalent ion always decreases the calculated concentration of the unionized part very much more rapidly than the addition of a salt with no common ion. It is difficult to see why the addition of silver nitrate should cause a depression in concentration of the un-ionized part of silver sulfate so much greater than that produced by potassium nitrate or magnesium nitrate; or why potassium bromate should cause a decrease in the concentration of the un-ionized part of barium bromate which is so much greater than that produced by potassium nitrate. When we turn to the rapid increase in the concentration of the un-ionized part caused by the addition of a salt with a common bivalent ion, we again find a result of the calculations which seems equally unreasonable. Such results cast serious doubts upon the significance of the calculated values of the un-ionized concentration. The most obvious explanation of them seems to be that *a part of what we have considered to be the un-ionized substance is in reality the intermediate ion,* such as $AgSO_4^-$ or NO_3Ba^+.

The possibility that intermediate ions exist in aqueous solutions of unibivalent salts has frequently been suggested in the literature, but has really received little serious consideration. In fact the authors who favor the assumption of intermediate ions have usually postulated a specific intermediate ion in order to account for some specific experimental result. Thus Abegg and Spencer,[1] in considering the solubility of thallous oxalate, assume that it gives rise to an intermediate ion, but that potassium oxalate does not. In the same way in a recent paper, Jellinek[2] concludes from calculations in regard to the freezing point that intermediate ions are present in sodium sulfate solutions, but not in potassium sulfate solutions.

It appears to the author highly probable that *all* unibivalent salts yield intermediate ions in not far from the same proportion at the same concentration if they are present in any of them; and it is his purpose to show that this hypothesis will explain in a general way the solubility relations of such salts, especially the abnormal increase in the solubility product, the extraordinary decrease in the calculated concentration of

[1] *Z. anorg. Chem.*, 46, 406 (1905).
[2] *Z. physik. Chem.*, 76, 309 (1911).

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the un-ionized part caused by the common univalent ion, and the peculiar effect of the common bivalent ion.

It may first be shown that it suggests an explanation of the increase produced in the solubility of very soluble salts by the addition of a salt with a common bivalent ion. Thus, the saturated solution of strontium nitrate (see curve in Fig. 4), which is about 6-normal, must have a large concentration of $SrNO_4^+$ ions and NO_3^- ions, but only a very small concentration of Sr^{++} ion. When strontium hydroxide is added to it, the ions which it brings into the solution are largely $SrOH^+$ and OH^-. As the amount of the common Sr^{++} ion introduced is small, the decrease of the concentration of the NO_3^- ion is small, and this effect is overcompensated by the amount of un-ionized $Sr(OH)NO_3$ formed by the combination of the $SrNO_3^+$ with the OH^-.

In the case of salts of moderate solubility, the main effect of the intermediate ion of the salt saturating the solution on the solubility will be that caused by the change in the proportion of this ion present, rather than that caused by the change in the formation of the un-ionized substance (such as $Sr(OH)NO_3$). There will be the further effect, when a salt with the common bivalent ion is added, of the intermediate ion of this added salt, which effect will consist in reducing the quantity of the bivalent ion which that salt brings into the solution. The direction of these effects can be predicted by formulating the mass-action equations as follows: Consider a salt A_2B which ionizes into the simple ions A^+ or A^- and $Ba^=$ or B^{++} and into the intermediate ion AB^- or AB^+. Let its molal solubility be S_0 in pure water, S_1 in the presence of another salt AC with the common univalent ion A^+ or A^-, and S_2 in the presence of another salt D_2B with the common bivalent ion $B^=$ or B^{++} and the intermediate ion DB^- or DB^+. Representing the molal concentrations of the constituents of the salt in the first solution by $(A_2B)_0$, $(A)_0$, $(B)_0$, and $(AB)_0$, and in the second and third solutions by $(A_2B)_1$ and $(A_2B)_2$, $(A)_1$ and $(A)_2$, etc., the following equations express the solubility principles[1] and the conditions of the problem:

$$(A_2B)_0 = (A_2B)_1 = (A_2B)_2. \qquad (1)$$

$$(A)_0(AB)_0 = (A)_1(AB)_1 = (A)_2(AB)_2. \qquad (2)$$

$$(A)_0^2(B)_0 = (A)_1^2(B)_1 = (A)_2^2(B)_2. \qquad (3)$$

$$S_0 = (A_2B)_0 + (AB)_0 + (B_0), \text{ and } S_1 = (A_2B)_1 + (AB)_1 + (B)_1; \qquad (4)$$

[1] Judging from the results with uni-univalent salts, the second and probably the third of these solubility principles may be expected to hold true approximately. The first principle, stating the constancy of the un-ionized concentration, is doubtless considerably in error; but the influence of this error on the result is comparatively slight, since that concentration forms a very small part of the total concentration. Its influence, so far as it goes, causes the decrease of solubility to be somewhat greater than that calculated from equations (6) and (7).

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or $2S_0 = 2(A_2B)_0 + (AB)_0 + (A)_0$, and

$$2S_2 = 2(A_2B)_2 + (ADB)_2 + (AB)_2 + (A)_2. \quad (5)$$

By combining these equations we obtain the following expressions for the fractional decrease in solubility produced by increasing the concentration of the univalent ion from $(A)_0$ to $(A)_1$ and by increasing that of the bivalent ion from $(B)_0$ to $(B)_2$:

$$S_0 - S_1 = \frac{(A)_1 - (A)_0}{(A)_1}\left[(B)_0\left(1 + \frac{(A)_0}{(A_1)}\right) + (AB)_0\right] \quad (6)$$

$$2(S_0 - S_2) = \frac{(B)_2^{1/2} - (B)_0^{1/2}}{(B)_0^{1/2}}\left[(A)_0\left(\frac{(B)_0}{(B)_2}\right)^{1/2} - (AB)_0\right] - (ADB)_2 \quad (7)$$

From these equations the following conclusions may be drawn:

(1) The opposit signs of the term $(AB)_0$ in the two expressions show that the intermediate ion AB would exert an opposit effect on the solubility, according as the concentration of the univalent ion or that of the bivalent ion is increased. In the former case it causes the decrease of solubility to be larger, and in the latter case to be smaller, than it would be if this intermediate ion were not present. In the latter case the intermediate ion DB also causes the decrease to be smaller, first, because of the effect of the negative term $(ADB)_2$, and secondly, because for a given concentration of the added salt, $(B)_2$ is smaller the larger the proportion of DB present.

(2) The solubility relations of a *slightly soluble* salt to which a salt with the *common univalent ion* A is added would not be much affected by the intermediate ion, since in this case $(AB)_0/(B)_0$ is small. This would still be true even when the concentration of the ion A is greatly increased, since the factor $\left(1 + \frac{(A)_0}{(A)_1}\right)$, by which $(B)_0$ is multiplied, can only vary between the limiting values 2 and 1.

(3) The solubility relations of a *slightly soluble salt* to which a salt with the *common bivalent ion* B is added will not be much affected by the intermediate ion AB so long as the concentration $(B)_2$ of the bivalent ion is not greatly increased, since in that case the ratio of $(AB)_0$ to $(A)_0(B)_0^{1/2}/(B)_2^{1/2}$ is small. If, however, the concentration of the bivalent ion be greatly increased, so that the latter term becomes small, the decrease of solubility may be considerably less than it would be if the intermediate ion were not present, even with a slightly soluble salt. The intermediate ion DB will also diminish the decrease of solubility more and more as the concentration of the added salt increases, owing to the larger proportion of the un-ionized substance ADB formed.

(4) In the case of *moderately soluble salts* the decrease of solubility caused by adding a salt with the *common bivalent ion* will pass over into an increase when the concentration of the added salt is moderately increased,

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for the ratio $(AB)_0/(A)_0$ is in this case fairly large and the negative term $(AB)_0$ within the bracket will soon compensate the steadily decreasing positive term containing $(A)_0$ to such an extent that the whole second member of equation (7) becomes negative, and this all the more since the negative term $(ADB)_2$ is also increasing.

(5) In the case of *readily soluble salts* to which a salt with the *common bivalent ion* is added, the first addition may cause an increase of solubility, for in a case where $(AB)_0/(A)_0$ is sufficiently large, the two negative terms may exceed the positive one, even when the factor of the latter $(B)_0^{1/2}/(B)_2^{1/2}$ is equal to unity.

(6) In the preceding statements about the different effects with salts of different solubility, it is assumed that there is a parallelism between the solubility and the proportion of the intermediate ion AB present. If in any special case this ion is present in larger proportion than usual, the salt will behave like one of higher solubility with normal ionization. (This seems to be true of lead chloride (and probably of lead iodate also), whose solubility is decreased much less than the usual amount by the addition of the common bivalent ion (Pb^{++}), and much more than the usual amount by the addition of the common univalent ion (Cl^-).)[1] It seems also to be true of calcium hydroxide.

A reference to the discussion in the preceding sections will show that the experimental results are in full accord with all these conclusions, and that they furnish illustrations of each one of them. The intermediate-ion hypothesis gives therefore a remarkably satisfactory explanation of these solubility phenomena from a qualitative or directional standpoint.

From a quantitative standpoint it is not possible to treat the matter very satisfactorily, owing to lack of knowledge of the proportions in which the intermediate ion and the simple ions are present. It seems worth while, however, to show that there are certain probable approximate assumptions which enable an estimate of these proportions to be made, and to illustrate by one or two examples the effect on the solubility relations of taking into account the presence of a considerable proportion of the intermediate ion.

There are two assumptions which seem to afford the best basis for estimating the proportions of the constituents in solutions of uni-bivalent salts. The first of these is the assumption that the principle that different salts of the same valence type have approximately the same ionization values, or more properly the same ionization constants,[2] applies to the

[1] When the curves representing the effect upon the solubility of lead iodate of adding potassium iodate was plotted on the drawing used in making Fig. 4, it was found that this curve fell considerably below the electrical limiting curve. It should be noted that these curves fall below the theoretical limiting curve only when the total ion concentration is small.

[2] Noyes, THIS JOURNAL, 30, 351 (1908).

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first stage of the ionization of unibivalent salts. Thus if a salt A_2B (such as Ag_2SO_4) ionizes at first into $A^+ + AB^-$, it ionizes as a uni-univalent salt, and should therefore be about 83 per cent. ionized in this way in 0.1 normal solution.

The second assumption is based on the fact that the transference numbers of unibivalent salts (excluding the halides of bivalent metals) vary scarcely at all with the concentration. It is a necessary consequence of this fact[1] that the intermediate ion, if it be present in considerable quantity, have an equivalent conductance equal to $\Lambda_A\Lambda_B/(2\Lambda_A+\Lambda_B)$, where Λ_A and Λ_B are the equivalent conductances of the simple univalent and bivalent ions of a salt A_2B.[2] Thus in the case o K_2SO_4, where Λ_{K^+} is approximately equal to $\Lambda_{SO_4^=}$, $\Lambda_{HSO_4^-}$ is nearly equal to $^1/_3\Lambda_{K^+}$.

Calculations of the concentration of the constituents in silver sulfate solutions were made by the writer, and in potassium sulfate solutions by Prof. W. C. Bray. The method used was to calculate by a method of approximations the concentrations of the constituents which under the

TABLE XVII.—CONCENTRATIONS OF THE CONSTITUENTS IN SOLUTIONS OF UNIBIVALENT SALTS CALCULATED UNDER CERTAIN ASSUMPTIONS AS TO THE INTERMEDIATE ION.

Silver Sulfate.			
Equiv. conc. of salt	0.01	0.05352	0.10
Conc. $Ag = \Sigma i$	0.00878	0.0403	0.0702
$AgSO_4$	0.00107	0.01004	0.02186
$SO_4^=$	0.00385	0.01513	0.02417
Ag_2SO_4	0.000077	0.001596	0.00397
$k_1 = (Ag^+)(NO_3^-)/(AgNO_3)$	0.123	0.254	0.336
$k_2 = (Ag^+)(SO_4^=)/(AgSO_4)$	0.0316	0.0608	0.0776
Per cent. sulfate as			
$AgSO_4^-$	21.4	37.50	43.7
$SO_4^=$	77.0	56.5	48.3
Ag_2SO_4	1.54	5.97	7.94
Potassium Sulfate.			
Equiv. conc. as salt	0.01	0.10	1.00
Conc. $K = \Sigma i$	0.0090	0.0774	0.62
KSO_4	0.0009	0.0176	0.25
$SO_4^=$	0.00405	0.0299	0.185
K_2SO_4	0.00005	0.0025	0.165
$k_1 = (K^+)(Cl^-)/(KCl)$	0.150	0.533	2.32
$k_2 = (K^+)(SO_4^=)/(KSO_4^-)$	0.040	0.132	0.46
Per cent. sulfate as			
KSO_4^-	18.0	35.2	46.0
$SO_4^=$	81.0	59.8	42.0
K_2SO_4	1.0	5.0	12.0

[1] Falk, THIS JOURNAL, 32, 1569 (1910). Noyes and Falk, *Ibid.*, 33, 1443 (1911).

[2] Lewis (THIS JOURNAL, 32, 1569 (1911) (footnote)) has shown that this follows from the hypothesis that the frictional resistance to the motion of the intermediate ion AB is equal to the sum of the resistances to the motion of the two constituent ions A and B.

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assumptions just stated cause the calculated specific conductance of the solution in each case to be the same as that experimentally determined. The results are given in Table XVII.

It will be seen from this table that the proportion of intermediate ion increases rapidly with increasing concentration. The most striking result, however, is that k_2, the ionization function for the second stage of ionization, increases with increasing ion concentration, and is nearly proportional to k_1. Since the latter is related to the total ion concentration (Σi) by the general equation which holds for diionic salts, $k_1 = K(\Sigma i)^{2-n}$, where K is a constant, it follows that k_2 must obey a similar law, though the exponent ($2-n$) will probably be somewhat different in the two cases. This uniformity in the functions may be regarded as a confirmation of the assumptions upon which the calculations were based.

Calculations were then made of the concentrations of the constituents in a 0.1 normal silver nitrate solution and in 0.1 normal potassium sulfate solution saturated with silver sulfate. The results are given in Tables XVIII and XIX:

TABLE XVIII.—CONCENTRATION OF THE CONSTITUENTS IN SOLUTIONS SATURATED WITH SILVER SULFATE.

Added salt.	Total Ag_2SO_4.	(Ag_2SO_4).	(Ag^+).	$(SO_4^=)$.	$(AgSO_4^-)$.	(NO_3^-) or (K^+).	$(AgNO_3)$ or (K_2SO_4).	(KSO_4^-).
None.....	53.52	3.19	40.3	30.26	10.04	0.0	0.0	0.0
99.60 mm. $AgNO_3$..	16.96	1.82	91.75	7.66	3.75	80.3	19.44	0.0
99.96 mm. K_2SO_4...	48.04	2.0	30.5	74.0	13.5	75.0	5.0	18.0

TABLE XIX.—VALUES OF THE UN-IONIZED CONCENTRATION AND THE SOLUBILITY PRODUCT IN SOLUTIONS OF SILVER SULFATE.

(All concentrations in milliequivalents per liter.)

Added salt.	Assuming intermediate ion. (Ag_2SO_4).	$(Ag^+)(AgSO_4^-)$.	$(Ag^+)^2(SO_4^=)$.	Assuming no intermediate ion. (Ag_2SO_4).	$(Ag^+)^2(SO_4^=)$.
(a) None.....	3.19	405.0	49100.0	17.02	48640.0
(b) 99.60 mm. $AgNO_3$..	1.90	366.0	64500.0	7.27	78500.0
Ratios b/a.....	0.57	0.90	1.30	0.43	1.61
(c) 99.96 mm. K_2SO_4...	2.0	41.2	68800.0	20.94	70160.00
Ratio c/a.....	0.63	1.02	1.40	1.23	1.44

The assumptions under which the calculations for Tables XVII to XIX were made do not define accurately the values which should be used, since the ionization constants for different uni-univalent salts are only approximately the same, and since the velocity of the intermediate ion could vary somewhat, though not greatly, without exerting a perceptible influence upon the values of the transference numbers. It should be understood, therefore, that the above calculations represent only very rough approximations. It would probably have been possible to have made these approximations more accurate by adopting certain auxiliary

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assumptions. One of the most valuable would have been to assume that the solubility products increase at about the same rate as in the case of uni-univalent salts for the same range of total ion concentrations. However, the object of the calculations was not to make accurate approximations, but to see if, on the basis of the assumptions which were chosen (see above), the behavior of the un-ionized concentration and of the solubility product would become less abnormal, and more in accord with what has been found for uni-univalent salts. An examination of Tables XVIII and XIX shows that the assumption of the presence of the intermediate ion in salts of the unibivalent type causes the abnormal increase in the un-ionized concentration when a salt with a common bivalent ion is added, to disappear, and in its place there is found to be a decrease comparable with that found for uni-univalent salts. If a salt with a common univalent ion is added the decrease in the un-ionized concentration becomes smaller when the presence of the intermediate ion is assumed, and in all cases the solubility product becomes more constant, as will be seen by a comparison of the ratios given in Table XIX. The effect of the assumption of the presence of intermediate ions in solutions of unibivalent salts is, therefore, to bring the behavior of the un-ionized concentration and of the solubility product into general accord with their behavior in solutions of uni-univalent salts.

25. Effect on the Solubility of Unibivalent Salts of a Substance with a Common Bivalent Ion Whose Own Intermediate Ion is Present in Large Proportion.

In discussing in the last section the effect on the solubility of a salt A_2B of another salt D_2B, its own intermediate ion DB was shown to exert an effect in the same direction as the intermediate ion AB; namely, that of causing the decrease of solubility to be smaller than it would be if no intermediate ion were present. It was also shown that either ion, when present in sufficient proportion, may cause the decrease of solubility to pass over into an increase. It may now be pointed out that this last effect might be produced by the intermediate ion DB in a way different from that described, if in any special case it is present in unusually large proportion. Thus referring to equation (7) above, it will be seen that $S_0 - S$ may change sign not only through a change in sign of the quantity within the bracket, but also through a change of sign of $(B)_2^{1/2} - (B)_0^{1/2}$. That is to say, there will be an increase of solubility in any case in which the salt D_2B has so large a value of the ratio $(DB)_2/(B)_2$ that the effect of adding it to the solution of the salt A_2B is to cause the B ion of the latter to unite with the D ion of the former to such an extent that the concentration of the B ion is decreased, rather than increased, by the added salt. That this may happen is clearly seen by considering the limiting case in which the salt D_2B dissociates only into the ions D and DB, in which

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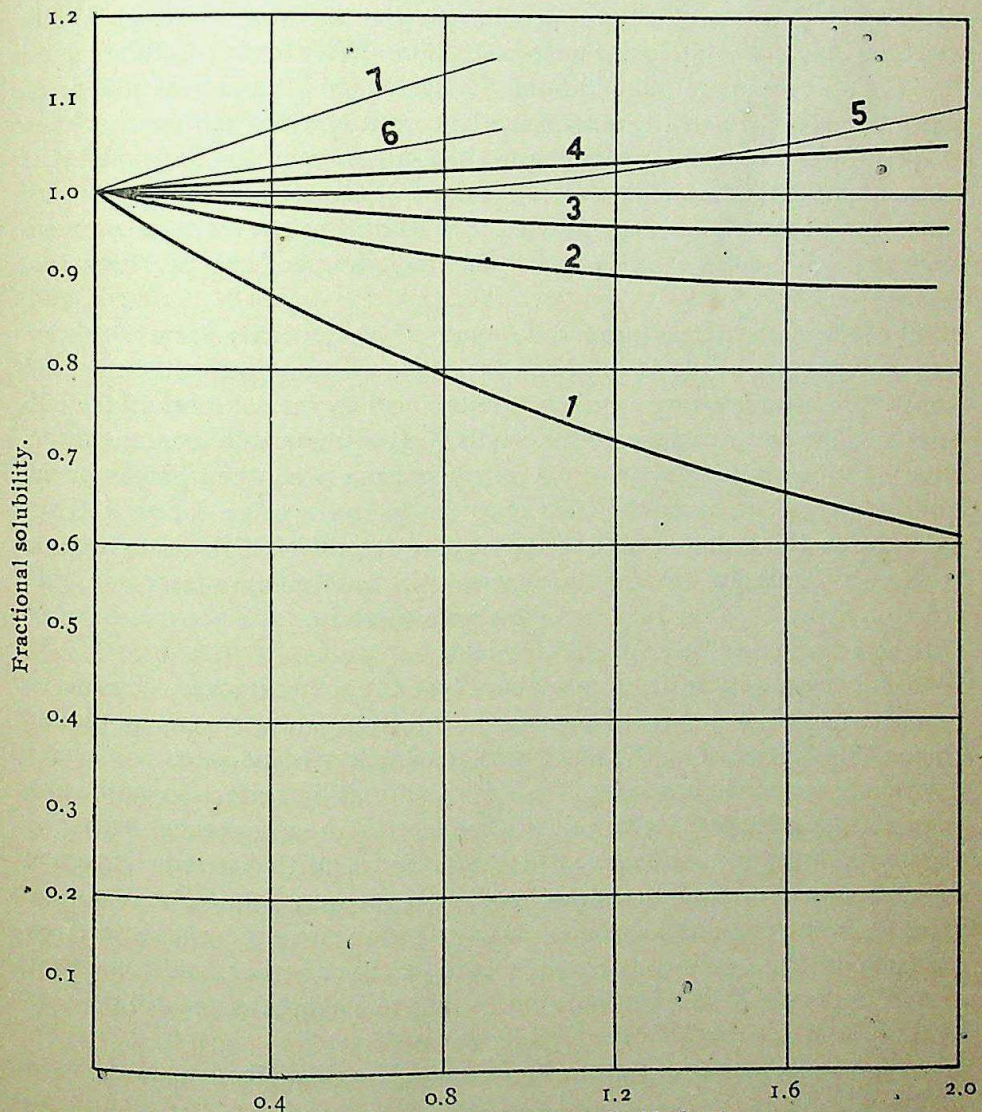
case the effect of adding it to a solution of the salt A_2B dissociated into the ions A and B would obviously be simply to convert the ion B into DB and thus increase the solubility.

This effect is well illustrated by the relative influences exerted on the solubility of silver sulfate by potassium sulfate, potassium hydrogen sulfate, and sulfuric acid. The fractional solubility[1] in the presence



1. Theoretical limiting curve.
2. $Ag_2SO_4 + K_2SO_4$.
3. $Ag_2SO_4 + KHSO_4$.
4. $Ag_2SO_4 + H_2SO_4$.
5. $Tl_2SO_4 + Na_2SO_4$.
6. $Tl_2SO_4 + NaHSO_4$.
7. $Tl_2SO_4 + H_2SO_4$.

Fig. 5.

[1] For the data see Paper V, Table II B.

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of these substances at different "fractional concentrations" is represented by the curves in Fig. 5, in which also the theoretical limiting curve corresponding to the assumption of complete ionization is plotted. It will be seen that the effect of potassium sulfate at all the concentrations (up to 0.1 normal) is to decrease the solubility, though very much less than the solubility-product principle would require; that that of potassium hydrogen sulfate is to cause a still smaller decrease; and that sulfuric acid produces an increase in the solubility. This marked difference in the effects of potassium sulfate and sulfuric acid is doubtless due to the different proportion of intermediate ion present in the solutions of these two substances. Thus, according to the estimate recorded in Table XVII, in 0.1 normal solution at 25° potassium sulfate consists of 35 per cent. of KSO_4^- and of 60 per cent. $SO_4^=$, and according to the estimate of Noyes and Stewart[1] sulfuric acid consists of about 67 per cent. of HSO_4^- and 27 per cent. SO_4^-.

The estimate of the latter investigators,[2] that in 0.1 formal solution the acid sulfate yields 34 per cent. $SO_4^=$, shows, moreover, that the addition of an equivalent quantity of sulfuric acid to the solution of the neutral sulfate causes under these conditions only a small increase in the $SO_4^=$ concentration, namely, an increase from 0.060 to 0.068 normal. From these data (and the fact that the quantity of un-ionized $MHSO_4$ present in this solution is 8 per cent. of the total $MHSO_4$) one may calculate by equation (7) that a neutral sulfate (M_2SO_4), whose solubility in water was 0.100 normal, would have a solubility 4.4 per cent. greater in a 0.1 normal solution of sulfuric acid.

Silver sulfate is a salt of only about half the solubility here considered, and its ionization is probably somewhat different from that of potassium or sodium sulfate; but the fact that its solubility is found to be about 5 per cent. greater in 0.1 normal sulfuric acid than in water shows that the general magnitude of the solubility effect is in accordance with that predicted from a consideration of the influence of the intermediate ion.

The effects of sodium sulfate, sodium hydrogen sulfate, and sulfuric acid on the solubility of thallous sulfate, for which the curves are also plotted in Fig. 5, bear the same relation to one another. All the curves have, of course, a higher position, owing to the greater solubility of the salt.

26. Summary of Papers V, VI and VII on Unibivalent Salts.

Paper V.—1. An accurate method for the analysis of bromates was described which consists in reducing the bromate to bromide by adding hydrazine hydroxide, acidifying with nitric acid, and precipitating as silver bromide.

[1] THIS JOURNAL, 32, 1133 (1910).
[2] *Loc. cit.*, p. 1159.

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2. The solubility of silver sulfate was determined at 25° in water and in solutions of magnesium nitrate, potassium nitrate, magnesium sulfate, potassium sulfate, and silver nitrate (see Tables I, II, and VII). The value for the solubility in water, 0.2676 mole per liter, is 4.1 per cent. higher than that obtained by Drucker (0.0257), and 0.86 per cent. lower than that obtained by Swan.

3. The solubility of barium bromate was determined at 25° in water and in solutions of magnesium nitrate, potassiun nitrate, barium nitrate, and potassium bromate (see Tables III, IV, and VII). The solubility in water was found to be 0.04018 equivalent per liter. This value is 0.63 per cent. higher than that found by Trautz and Anschütz.

4. The solubility of lead chloride at 25° was determined in water and in solutions of lead nitrate. The solubility in water was found to be 0.07776 equivalent per liter, which is 0.08 per cent. higher than the value found by Noyes.

5. The conductance of all the solutions was measured at 25°. The values for the conductance and ionization of the salts are given in Tables VIII to XI.

6. The solubilities of the salts were plotted as ordinates, and the equivalent concentrations of the added salts as abscissas, and the solubility curves were found to belong to three types, as follows:

a. When a salt containing a common univalent ion is added, the solubility decreases rapidly, and the curve is qualitatively of the form to be expected from the solubility-product principle.

b. When a salt containing a common bivalent ion is added the change in solubility is altogether different from what would be expected from the solubility-product principle. The solubility of moderately soluble salts at first decreases slightly and then increases as the concentration of the added salt increases. With less soluble salts, such as barium bromate, the decrease is continuous, though slight, up to a concentration of 0.2 normal for the added salt. With extremely soluble salts the solubility increases from the beginning with increase in the concentration of the bivalent ion, and the curve is therefore of the form (*c*) which is found when a salt with no common ion is added.

c. When a salt with no common ion is added the solubility always increases. The rate of increase depends upon the degrees of ionization of the salts concerned in the metathesis which results from the mixing of the salts.

7. The addition of potassium hydrogen sulfate decreases the solubility of silver sulfate less than the addition of potassium sulfate, and the decrease caused by the latter is slight. Sulfuric acid increases the solubility. The curve in the latter case is intermediate between the curves for a common ion and those for no common ion.

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8. The addition of magnesium sulfate decreases the solubility of silver sulfate less than the addition of potassium sulfate.

9. The solubility relations of bivalent salts are expressed by two types of curves, that for the addition of a common ion and that for the additon of a salt with no common ion.

10. While the solubility curves for the addition of a salt with a common bivalent ion to a very soluble unibivalent salt are of a form altogether different from what would be expected from the solubility-product principle, it is shown that the curves for the less soluble salts are approaching the theoretical form.

Paper VI.—11. The solubility of barium iodate in water at 25° was found to be 0.001579, and of lead iodate 0.0001102 equivalent per liter.

12. The solubility of barium iodate was determined in solutions of potassium nitrate, barium nitrate, and potassium iodate.

13. The solubility of lead iodate was determined in solutions of potassium nitrate, lead nitrate, and potassium iodate.

14. When a salt with a common bivalent ion is added to solutions of these slightly soluble salts, the solubility curves are very nearly of the theoretical form in the more dilute solutions.

15. When a salt with a common univalent ion is added, the solubility of these salts decreases with extreme rapidity, and when a salt with no common ion is added, the solubility increases rapidly.

16. The solubility curves for the addition of a common ion are shown to assume practically the same form as those for the addition of a salt with no common ion in the case of *very soluble salts*, like strontium nitrate.

Paper VII.—17. The concentrations of the un-ionized part and of the ions of the salt saturating the solution were calculated for all of the mixtures from the ionization of the salts in pure water under the assumption that the only ions present are the simple ions. The results are given in Tables I to IV.

18. The solubility product for these unibivalent salts increases far more rapidly than that for uni-univalent salts (see Tables V to VIII, Figs. 1 to 3). It increases rapidly, whatever the type of the added salt; but the increase is somewhat more rapid when the common ion added is univalent than when it is bivalent. The rate of the increase may be expressed (for a salt A_2B) by equations of the form

$$(A)^2(B) = k(\Sigma i)^{m_i}, \text{ or } \log (A)^2(B) = m_i \log (\Sigma i) + \log k_i.$$

In these equations m_i has, for ion concentrations between 0.03 and 0.10 normal, an average value of about 0.45 when the common ion added is univalent, and one of about 0.34 when it is bivalent. The solubility product remains more nearly constant the smaller the solubility of the salt.

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19. The decrease in the concentration of the un-ionized part of a univalent salt, caused by adding another salt to its saturated solution, is shown to be very much more rapid than the decrease in the solubility of a non-electrolyte caused in the same way. When the salt saturating the solution is unibivalent the decrease in the concentration of the un-ionized part is greater when a salt with a common univalent ion is added than the similar decrease observed for uni-univalent salts. When a salt with no common ion is added the decrease in the concentration of the un-ionized part is much less rapid, and when a salt with a common bivalent ion is added, there is an increase instead of a decrease. The increase in the concentration of the un-ionized part when a common bivalent ion is added becomes smaller as the solution becomes more dilute, while the decrease in the un-ionized part caused by the common univalent ion becomes larger as the concentration of the solution decreases.

20. The results are expressed by equations of the form

$$(A_2B) = k_u(\Sigma i)^{m_u}; \text{ or } \log (A_2B) = m_u \log (\Sigma i) + \log k_u.$$

The values of m_u are shown to be very irregular and to depend in an extraordinary degree on the type of ion added to the solution.

21. The solubility effects produced by adding a common ion have also been discussed in another way, namely, by expressing the concentrations both of the salt saturating the solution and of the added salt in terms of the solubility of the former salt in pure water. Curves have been presented in Fig. 4 which show the change of this "fractional solubility" with the "fractional concentration" of the added salt in relation to the solubility of the salt saturating the solution and the type of the added salt, and in relation to the "theoretical limiting curve" representing the solubility decrease under the assumption that both salts are completely ionized. The actual curves lie in general not far above the limiting curve when the common univalent ion is added, whatever be the solubility. The curves for the addition of the common bivalent ion lie near the limiting curve for very slightly soluble salts, like lead iodate; but they deviate more and more from it as the solubility increases, finally approaching the position of the curves for the addition of a salt with no common ion.

22. Lead chloride in its solubility relations behaves like a salt of greater solubility. This is probably related to its abnormal ionization, which is indicated by the unusually small value of its conductance ratio.

23. The irregular variation of the un-ionized part, the abnormal increase in the solubility product, and the abnormal form of the solubility curve for the addition of the common bivalent ion are remarkable results which require some general explanation.

24. The simplest hypothesis which brings these results into harmony with each other and with the behavior of uni-univalent salts is that all

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unibivalent salts dissociate in two steps, and therefore give rise to an intermediate ion of the type KSO_4^- or $BaNO_3^+$. As a general explanation of the solubility phenomena, this is believed to be a new suggestion. Previous assumptions of the existence of the intermediate ion had been made only in specific cases and to explain abnormal results which were believed to be quite specific in their nature. It is here assumed that the proportion of the intermediate ion increases with the concentration, and that it has in general roughly the same value for salts of the same valence type at any given concentration.

25. It is shown that this hypothesis leads to a number of definit deductions as to the direction and general magnitude of the changes in the solubility of unibivalent salts produced by the addition of other salts with both a common univalent and a common bivalent ion; and it is shown that these conclusions are in complete accord with the experimental values. The demonstrated correspondence of these deductions with the facts is thought to constitute the most important theoretical result of these investigations. The deductions are not reproduced here as they have already been stated in summarized form in the paragraphs numbered (1) to (6) in Section 24.

26. Two principles are suggested, by a combination of which the proportion of the intermediate ion present in solutions of unibivalent salts may be approximately determined; and the results of calculations are presented (in Tables XVII and XVIII), showing the concentration of the different constituents in certain solutions of silver sulfate and of potassium sulfate, and in saturated solutions of silver sulfate containing also silver nitrate and potassium sulfate. It is shown (in Table XIX) that the solubility product $(Ag^+)^2(SO_4^=)$ remains much more nearly constant, and that there is a normal decrease instead of the abnormal increase in the concentration of the un-ionized part for the case where a salt with a common bivalent ion is added, when the presence of the intermediate ion is taken into account.

27. It is shown that the facts that potassium sulfate decreases and that sulfuric acid increases the solubility of silver sulfate are explained by the consideration that the proportion of the intermediate ion HSO_4^- present in the acid solution is much larger than the proportion of the intermediate ion KSO_4^- present in the potassium sulfate solution. A quantitative estimate of the effect that should be exerted by sulfuric acid on the solubility of a neutral sulfate of moderate solubility is shown to be in agreement with that observed in the case of silver sulfate.

In conclusion, I wish to thank Professor A. A. Noyes for many helpful suggestions in regard to this work on unibivalent salts; and especially for his revision of the theoretical part of the seventh paper. I wish also to thank Professor W. C. Bray for suggestions in connection with the cal-

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culations. Grateful acknowledgments are also due to the Carnegie Institution of Washington, whose financial assistance has made this work possible.

BOSTON, MASS.

[CONTRIBUTIONS FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

AN EQUILIBRIUM IN THE COBALTAMMINES.[1]

BY ARTHUR B. LAMB AND JOHN W. MARDEN.

Received July 20, 1911.

The ammonia compounds of cobalt salts, called the *cobaltammines* to distinguish them from the organic amines, constitute an unusually interesting group of substances. A great number of them have been prepared; they have been arranged in numerous well defined classes, and the systematic correlation of these classes has been well worked out. They exhibit points of marked similarity with organic substances; thus they contain complex radicals entirely analogous in their behavior to organic radicals; they exhibit structural and stereomeric isomerism quite as striking as that of many organic substances; substitutions can be made with an even greater freedom than in organic compounds. On the other hand, these compounds are distinctly inorganic; they are for the most part salts, more or less soluble in water, and more or less electrolytically dissociated.

These unusual substances offer particular advantages for the study of such fundamental chemical problems as valency, the connection between chemical nature and electrolytic dissociation, etc. Indeed, they have already given rise to one theory of valency (Werner's), which, even if it may ultimately prove incorrect, has nevertheless furnished a simple and comprehensive correlation of this group and of other similar groups. However, for a study of any of these problems a knowledge of the *energetic* relationships is important. We ought, for instance, to know the difference in the total and free energy of formation of the different isomers and part isomers in this group; or, if possible, the difference in free or total energy between a partial and principal valency in the sense of Werner's theory. There is at present no information whatever on these subjects, and it was in the hope of making good some of this deficiency that this research was undertaken.

The most promising point of attack appeared to be the spontaneous transformations which many of the cobaltammines undergo either in the dry state or in solution. If these transformations could be shown to approach equilibria, the free energy change, or the affinity of the reactions,

[1] Presented at the June, 1911, meeting of the New York Section of the American Chemical Society.

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would be known; if the equilibria could be measured at two different temperatures, or if an independent measurement of the heat of reaction could be made, then the total energy change could be calculated.

Of these transformations the one which has been longest known is the change of the *purpureo* salts into *roseo* salts in aqueous solution. In this paper we shall hope to show that a reversible equilibrium is here attained. At a later date we shall hope to furnish the further data necessary for a calculation of the total energy change.

The Transformation of Purpureo Salts into the Corresponding Roseo Salts and Vice Versa.

Purpureo and roseo cobalt chloride are both trichloropentammine compounds of cobalt. They were among the original cobaltammines prepared by Genth[1] in 1851. Claudet[2] and Fremy[3] prepared the same substances independently a little later. Gibbs and Genth[4] in 1856 found that these trichloropentammine salts, which till then had all been called roseo salts, really consisted of *two* classes of salts. To one class they gave the old name roseo cobaltammines; to the other, because of the characteristic color of its compounds, they gave the name purpureo cobaltammines. They pointed out that the purpureo salts were in general less soluble in water than the roseo salts; that roseo chloride contained one equivalent of water, while purpureo chloride contained none; and that the purpureo radical behaved as a di-acid, the roseo radical as a tri-acid base. Fremy,[5] and Gibbs and Genth[6] had observed the fact that the chlorine in the purpureo salts was not completely precipitable by silver nitrate in the cold, but Krock[7] first established the fact that it was *exactly* one-third of the chlorine and therefore only one of the chlorine atoms which could not be precipitated.

All these facts, amply confirmed by Jörgensen, are expressed from Werner's point of view by the two following formulas:

$$\left[\begin{matrix} Cl \\ Co \\ (NH_3)_5 \end{matrix}\right] Cl_2 \qquad\qquad \left[\begin{matrix} H_2O \\ Co \\ (NH_3)_5 \end{matrix}\right] Cl_3$$

Purpureo pentammine cobalt chloride. Roseo pentammine cobalt chloride.

Only the chlorine atoms outside the radical can function as ions; only two-thirds, then, of the total chlorine in the purpureo salt can be pre-

[1] Nordamerikanischer Monatsbericht für Natur- und Heilkunde, 1, Jan., 1851.

[2] *Ann. chim. phys.*, 23, 483.

[3] *Compt. rend.*, 32, 509, 808.

[4] "Researches on the Ammonia Cobalt Bases." Smithsonian Contributions to Knowledge. (Washington, 1856.)

[5] *Ann. chim. phys.*, 3, 35, 303.

[6] *Loc. cit.*, p. 5.

[7] Lunds. Univers. Arsskrift, 1870.

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cipitated by silver nitrate, while all of it in the roseo salt can be. The purpureo ion is therefore divalent, the roseo trivalent.

Gibbs and Genth[1] observed the easy conversion of roseo salts into the corresponding purpureo salts when heated in aqueous solution, and especially when heated in hydrochloric acid, or in a solution of ammonium chloride.

Jörgensen[2] was the first to observe the reverse change, that is, the change of purpureo into the roseo salt; he found that this took place simply on standing in aqueous solution. The process was a slow one in the case of the chloro, but more rapid in the case of the nitrato salts.[3] Werner and Miolati,[4] in measuring the conductivity of solutions of various purpureo salts, found an increase in conductivity with the time, which indicated a conversion into roseo salts, thus confirming the observations of Jörgensen. Jörgensen also found that while hydrochloric acid and the alkali chlorides readily converted roseo chloride into purpureo chloride, silver oxide, barium hydroxide and ammonia, when not boiled, converted purpureo salts into roseo. If boiled, decomposition of the ammine set in.

Finally, it has been found in this laboratory that in *concentrated* aqueous solution, even at room temperature, roseo chloride is converted into purpureo chloride.

We may summarize these results as follows: In dilute aqueous solutions at low and moderate temperatures and especially in alkaline solutions, purpureo salts change to roseo; in concentrated solutions, or in solutions containing chlorides, or on heating, the reverse change takes place. The evidence, therefore, strongly indicated the existence of a true equilibrium between the roseo and the purpureo modification. In order to study this equilibrium intelligently, it was evidently necessary to know something about the velocity of transformation under different conditions. We therefore first directed our attention to this aspect of the problem, and in particular, since it takes place under the more convenient conditions, to the transformation of purpureo salts into roseo.

The Velocity of Transformation of Purpureo Salts Into Roseo Salts.

Since in the purpureo salts only two-thirds of the negative radical can become ionized, while in the roseo salts all of it can be, it follows that the conductivity of a solution of purpureo chloride, for instance, must increase as the purpureo chloride changes into roseo chloride, provided the mobilities of the two complex ions are approximately the same. Indeed, it was largely upon the measurements of the electrical conductivities of these and similar cobaltammines that Werner based

[1] *Loc. cit.*, p. 9.
[2] *J. prakt. Chem.*, 19, 51 (1879).
[3] *Ibid.*, 19, 232 (1879).
[4] *Z. physik. Chem.*, 14, 520 (1894).

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his theory of the structure of these compounds. The transformation would be represented as follows:

$$\left[\begin{matrix} & Cl \\ Co & \\ & (NH_3)_5 \end{matrix}\right] Cl_2 + H_2O \longrightarrow \left[\begin{matrix} & H_2O \\ Co & \\ & (NH_3)_5 \end{matrix}\right] Cl_3,$$

or in very dilute solution, where ionization could be assumed to be complete, as follows:

$$\left[\begin{matrix} & \dot{C}l \\ Co & \\ & (NH_3)_5 \end{matrix}\right]^{++} + 2Cl^- + H_2O \longrightarrow \left[\begin{matrix} & H_2O \\ Co & \\ & (NH_3)_5 \end{matrix}\right]^{+++} + 3Cl^-.$$

The increase in conductivity would evidently amount to 50 per cent. of the original conductivity, assuming an equal percentage dissociation and equal mobilities of the complex ions. This increase is large enough to permit of accurate measurement, and we therefore chose this method for determining the progress of the transformation.

We have assumed in our calculations that the increase in molecular conductivity is *exactly* proportional to the amount of transformation, that is, that $\frac{\mu_t - \mu_0}{\mu_\infty - \mu_0}$ equals the fraction transformed, where μ_0, μ_t and μ_∞ represent respectively the molecular conductivity at the beginning, at the time t and at the end. This must be very nearly the case, for even if the percentage dissociation, or the percentage hydrolysis of the two salts, or the mobilities of the two ions were different, their effect on the conductivity would be nearly proportional to the relative concentration of the two salts. The solutions used were very dilute (1/500 molar); the percentage dissociation must have been nearly the same. The measurements of Werner and Miolati have also shown that the mobilities of the purpureo and roseo ions must be nearly identical.

The solutions were prepared by dissolving a weighed quantity (always less than 1 gram) of the desired salt in exactly one liter of redistilled water previously warmed to precisely 25° (its specific conductivity varied between 1.08 and 2.5×10^{-6} 1/ohms), and shaking vigorously until solution was complete. The temperature was again adjusted exactly, and the solution poured rapidly into the dry conductivity cells already fixed in the thermostat, up to a mark on the narrow neck of the cells. Duplicate runs were made, usually in different cells. The salts were prepared according to the improved methods of Jörgensen.[1] The salts were finely ground before use; nevertheless they went into solution rather slowly, the most insoluble sometimes requiring twenty minutes, the most soluble four or five minutes. Most of the salt would, however, always dissolve in two or three minutes, and the time was therefore counted from one to three minutes after the addition of the salt. Conductivity measurements were taken within a few minutes after complete solution.

[1] *Z. anorg. Chem.*, 17, 160.

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The measurements were made with a Kohlrausch spirally-wound bridge permitting a reading on the bridge wire to one part in ten thousand. A thermostat maintained a temperature of 25° constant to within a few hundredths of a degree. A thermometer which could be read to 0.01° was nevertheless fitted in the large, closed, flask-shaped cells, and the temperature at each reading of the conductivity recorded. The electrodes were firmly fixed in a permanent position and provision was made for stirring.

The following tables contain the result of the velocity measurements. In them the time and the corresponding molecular conductivities are given; when substances other than the cobaltammines were present in the solution the specific conductivities are also given. In the last column of each table are given the values of K, a constant calculated for a first-order reaction, that is, according to the expression

$$K = 1/t \log \frac{\mu_t - \mu_0}{\eta_\infty - \mu_0}.$$

The values of μ_0 and μ_∞ were obtained by extrapolation. It will be seen that these values agree well with one another in the different comparable series.

TABLE I.—VELOCITY OF TRANSFORMATION OF A 0.004 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(259.7)	...	1580	281.3	0.067
40	260.3	0.062	1940	284.3	0.063
345	263.3	0.046	2240	285.5	0.058
470	265.8	0.058	2810	289.3	0.054
790	271.3	0.067	∞	(360.0)	...
1355	278.3	0.066			

Mean value $K = 0.060 \times 10^{-3}$.

TABLE II.—0.002936 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT NITRATE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(253.0)	...	205	256.2	0.054
25.5	253.4	0.043	275	257.0	0.051
55	254.0	0.058	1138	267.8	0.049
108	255.2	0.070	∞	(376.0)	...
185	256.2	0.060			

Mean value $K = 0.055 \times 10^{-3}$.

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TABLE III.—0.002978 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT NITRATE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(244.0)	...	159	245.4	0.031
39	244.7	0.064	316	248.8	0.055
61	244.9	0.051	496	250.5	0.048
81	245.3	0.057	633	252.9	0.052
91	246.1	0.082	1402	263.8	0.054
			∞	(363.9)	...

Mean value $K = 0.055 \times 10^{-3}$.

TABLE IV.—0.003266 MOLAR SOLUTION OF BROMOPENTAMMINE BROMIDE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(259.5)	...	196	270.2	0.177
23	260.8	0.174	241	272.0	0.166
28	260.7	0.143	255	272.0	0.157
33	261.5	0.188	575	287.2	0.163
38	261.9	0.155	1311	313.0	0.156
43	262.1	0.184	2030	336.5	0.166
50	262.6	0.190	2713	350.6	0.163
144	267.9	0.183	∞	(402.0)	...

Mean value $K = 0.169 \times 10^{-3}$.

TABLE V.—0.003266 MOLAR SOLUTION OF BROMOPENTAMMINE COBALT BROMIDE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(258.2)	...	255	271.5	0.167
34	260.1	0.165	575	287.2	0.171
44	261.0	0.186	1310	314.5	0.164
51	261.1	0.169	2031	338.1	0.177
145	266.2	0.169	2710	353.1	0.177
197	268.7	0.169	∞	(402.0)	...
240	271.0	0.165			

Mean value $K = 0.170 \times 10^{-3}$.

TABLE VI.—0.002758 MOLAR SOLUTION OF NITRATOPENTAMMINE COBALT NITRATE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(262.4)	...	181	292.2	0.745
25	267.1	0.744	333	310.6	0.755
30	269.8	0.980	423	320.2	0.753
56	273.1	0.784	1015	358.3	0.849
60	273.6	0.800	1383	364.2	0.764
82	276.4	0.704	1658	367.2	0.733
98	279.1	0.728	2530	372.4	0.739
120	281.8	0.675	∞	(374.0)	...
151	287.1	0.729			

Mean value $K = 0.76 \times 10^{-3}$.

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TABLE VII.—0.002949 MOLAR SOLUTION OF NITRATOPENTAMMINE COBALT NITRATE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(260.0)	..	638	346.7	0.72
14	263.5	0.83	1358	379.3	0.73
24	265.2	0.72	1478	381.1	0.71
43	270.2	0.81	1607	383.3	0.71
100	279.5	0.69	1838	386.5	0.71
199	296.8	0.71	2678	391.6	0.74
260	304.1	0.67	∞	(393.0)	..
365	323.5	0.79			

Mean value $K = 0.73 \times 10^{-3}$.

TABLE VIII.—0.002949 MOLAR SOLUTION OF NITRATOPENTAMMINE COBALT NITRATE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(255.5)	..	365	329.4	0.99
7	257.6	(1.14)	638	345.2	0.78
16	258.6	0.73	1358	376.2	0.81
23	260.9	0.83	1479	378.1	0.80
45	264.3	0.69	1606	380.4	0.84
73	271.3	0.78	1839	382.4	0.81
198	290.0	0.68	2676	385.5	0.77
260	298.6	0.67	∞	(387.9)	..

Mean value $K = 0.79 \times 10^{-3}$.

TABLE IX.—0.007982 MOLAR SOLUTION OF NITRATOPENTAMMINE COBALT NITRATE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(247.3)	..	173	277.7	0.77
20	251.4	0.79	258	289.7	0.77
29	253.0	0.76	380	304.4	0.78
64	259.0	0.72	1243	336.9	0.52
107	267.0	0.76	∞	(363.0)	..
123	270.1	0.77			

Mean value $K = 0.76 \times 10^{-3}$.

TABLE X.—0.003012 MOLAR SOLUTION OF NITRATOPENTAMMINE CHLORIDE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(254.5)	..	67	270.0	0.73
10	257.0	0.76	145	287.7	0.78
20	259.8	0.81	223	301.5	0.76
24	260.8	0.80	516	340.7	0.75
28	262.0	0.82	1435	389.1	0.79
48	266.5	0.78	∞	(400.0)	..

Mean value $K = 0.78 \times 10^{-3}$.

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TABLE XI.—0.002651 MOLAR SOLUTION OF NITRATOPENTAMMINE COBALT NITRATE IN 0.001 MOLAR SOLUTION OF NITRIC ACID AT 25.°

Time. Minutes.	Specific conductivity 1/ohms.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	0.0	(260.0)	..
11	0.000658	263.8	(1.21)
33	0.000665	266.6	0.71
74	0.000683	273.8	0.68
127	0.000709	284.3	0.73
150	0.000717	287.5	0.71
179	0.000735	294.6	0.74
262	0.000758	303.9	0.71
1144	0.000916	367.2	0.72
1222	0.000919	368.3	0.69
1320	0.000926	371.3	0.70
1505	0.000935	374.9	0.69
2610	0.000959	394.4	0.70
∞	....	(386.3)	..

Mean value $K = 0.71 \times 10^{-3}$.

The specific conductivity of the ammine was obtained by subtracting the specific conductivity of the nitric acid from the observed specific conductivity.

TABLE XII.—0.002640 MOLAR SOLUTION OF NITRATOPENTAMMINE COBALT NITRATE IN 0.002 MOLAR SOLUTION OF NITRIC ACID AT 25°.

Time. Minutes.	Specific conductivity 1/ohms.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	.....	(260.0)	..
40	0.000685	267.6	0.65
70	0.000696	271.9	0.59
106	0.000704	275.0	0.50
136	0.000724	282.8	0.61
154	0.000728	284.4	0.59
289	0.000774	302.3	0.59
319	0.000781	305.1	0.58
349	0.000794	310.1	0.60
379	0.000802	313.3	0.60
1047	0.000907	354.3	0.54
1124	0.000918	358.6	0.55
∞	.....	(390.0)	..

Mean value $K = 0.58 \times 10^{-3}$.

TABLE XIII.—0.002644 MOLAR SOLUTION OF NITRATOPENTAMMINE COBALT NITRATE IN 0.0146 MOLAR SOLUTION OF SODIUM ACETATE AT 25°.

Time. Minutes.	Specific conductivity 1/ohms.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	.....	...	..
12	0.000572	222.1	0.66
14	0.000572	222.1	0.56
24	0.000574	224.0	0.69

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TABLE XIII (*continued*).

Time. Minutes.	Specific conductivity. 1/ohms.	Molecular conductivity. 1/ohms.	$K \times 1000$.
36	0.000580	226.2	0.74
44	0.000583	227.4	0.73
57	0.000586	228.6	0.66
69	0.000591	230.6	0.69
77	0.000595	232.1	0.71
87	0.000599	234.6	0.78
99	0.000603	235.2	0.71
110	0.000604	235.6	0.66
117	0.000606	236.4	0.66
192	0.000625	244.8	0.64
222	0.000631	246.1	0.59
299	0.000650	255.9	0.64
391	0.000669	261.0	0.59
599	0.000705	275.0	0.58
1364	0.000769	300.0	0.52
1970	0.000805	314.1	0.64
2880	0.000817	318.7	0.73
∞	....	(319.5)	..

Mean value $K = 0.66 \times 10^{-3}$.

TABLE XIV.—SUMMARY OF RESULTS OF VELOCITY EXPERIMENTS AT 25° IN AQUEOUS SOLUTIONS.

No.	Substance.	Concentration molar.	Third substance conc. molar.	Constant $K \times 1000$.
1	$[Co(NH_3)_5Cl]Cl_2$	0.004000	..	0.060
2	$[Co(NH_3)_5Cl](NO_3)_2$	0.002936	..	0.055
3	"	0.002978	..	0.055
4	$[Co(NH_3)_5Br]Br_2$	0.003266	..	0.169
5	"	0.003266	..	0.170
6	$[Co(NH_3)_5NO_3](NO_3)_2$	0.002758	..	0.76
7	"	0.002949	..	0.73
8	"	0.002949	..	0.79
9	"	0.007982	..	0.76
10	$[Co(NH_3)_5NO_3]Cl_2$	0.002918	..	0.78
11	$[Co(NH_3)_5NO_3](NO_3)_2$	0.002651	0.001 HNO_3	0.71
12	"	0.002640	0.002 HNO_3	0.58
13	"	0.002644	0.0146 NaAc	0.66

These experiments show that the change from purpureo is very slow at these concentrations; slow enough to permit of an accurate analytical determination of the relative amounts of roseo and purpureo salts in a given solution at 25°. This was the immediate information desired from these experiments. Nevertheless other interesting relations were found, as follows:

The change to the roseo is a *monomolecular* one. The variations in the constant are relatively small. This indicates that the change is either a slow intramolecular change or a slow process of electrolytic dissociation.

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The salts which were studied differ decidedly in their rates of transformation; the bromo changes about three times, the nitrato about ten times as fast as the chloro salt. These differences are much greater than the differences in electrochemical potential of the chlorine, bromine or nitrate ion, or in the differences in the volume of the chlorine, bromine or nitrate radical. However, the stability of the oxalato, carbonato and nitrito pentammine salts indicates that less acidic radicals leave in complex less readily than the more acidic ones.

The rate of transformation is independent of the negative group outside the complex radical; the velocity constants for the chloro chloride and the chloro nitrate are identical within the experimental error (Nos. 1, 2 and 3) and so are the velocity constants for the nitrato nitrate and the nitrato chloride (Nos. 6, 7, 8 and 10).

The velocity constant is independent of the original concentration of the reacting substances, as would be expected for a first order-reaction (Nos. 6, 7, 8 and 9).

The rate of transformation is also nearly, if not quite, independent of the hydrogen ion concentration. Thus the constant for the nitrato nitrate in pure water, 0.001 and 0.002 molar nitric acid and in 0.0146 sodium acetate differed but slightly (Nos. 6, 7, 8, 11, 12 and 13). This is markedly different from the behavior of green chromium chloride solutions, where the rate of transformation to violet chromium chloride was found to be very decidedly dependent on the hydrogen ion concentration.[1]

These experiments on the velocity of transformation showed clearly that equilibrium would not be reached at 25° within a feasible time. We therefore attempted to measure the rate of transformation in a similar fashion at the boiling point of water. We immediately found that decomposition of the cobaltammines occurred within a few moments under these conditions and within a few hours at 70°. It was evident that unless this decomposition could be avoided the equilibrium conditions would become hopelessly complicated. The decomposition of the purpureo salts in aqueous solution was therefore next studied.

The Decomposition of Pentammine Cobalt Salts in Aqueous Solution.

It was observed in the above cases where cobaltammine solutions were heated to 100° or thereabouts that no decomposition was visible for some time, but that suddenly a black precipitate appeared and then decomposition progressed to apparent completion in a few moments, the black precipitate forming in large quantities and leaving an almost colorless supernatant liquid. When the solution was acid, the appearance of the black precipitate was delayed, but once it had appeared decomposition progressed to apparent completion with equal suddenness. A series of experiments was carried out to test the effect of different concentrations

[1] Lamb, THIS JOURNAL, 28, 1710 (1906).

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of acid on this decomposition. In these experiments weighed quantities of purpureo cobalt chloride were added to a given volume of the different solutions of hydrochloric acid heated to 100° in a water bath. The results are recorded in Table XV.

TABLE XV.—RATE OF DECOMPOSITION OF SOLUTIONS OF CHLOROPENTAMMINE COBALT CHLORIDE AT 100°.

No.	Concentration of salt. Molar.	Concentration of HCl. Molar.	Time of appearance of black ppt. Minutes.	Retardation. Minutes.	Retardation per equivalent acid. Minutes.	Remarks.
1.....	0.00966	0	15	0	0	
2.....	0.00948	0.0050	28	13	2.6	
3.....	0.01004	0.0100	45	30	3.0	
4.....	0.00942	0.0133	108	93	6.9	
5.....	0.00966	0.0200	155	140	7.0	
6.....	0.00965	0.0244	315	300	12.3	
7.....	0.00968	0.0400	780	765	19.1	
8.....	0.00968	0.0800	..	..	..	No apparent decomposition after many hours

The decomposition of the cobaltammine liberates five equivalents of ammonia, and the appearance of the black precipitate (doubtless a hydrated hydroxide of cobalt) marks the point at which this decomposition has produced a certain alkalinity in the solution; once this alkalinity has been attained the decomposition becomes very rapid. If the solution originally contained acid this will require neutralization, and the appearance of the black hydroxide will be retarded; the greater the concentration of the acid the greater the retardation. If the amount of acid originally present is more than equivalent to the ammonia liberated, then the decomposition will proceed to completion without the formation of any hydroxide. These conclusions are all confirmed by the experiments in the above table.

The retardation per equivalent of acid is much greater in the concentrated acid solutions than in the dilute ones. There is then apparently a specific retarding effect of the acid. This cannot, however, be a very marked effect, for the greater retardation must be in part due to the lesser concentration of the cobaltammine in the partially decomposed solution.

This method of following the decomposition is evidently too indirect to be satisfactory. Since ammonia is liberated by the decomposition of the ammine, any method of following the changing acidity of the solution would tell the extent of decomposition at that time. The various indicators which were tried proved to be very unsatisfactory on account of the deep color of the solution. The addition of solid barium carbonate was tried as a means of determining the acidity, but a blank test showed that this simply caused the complete hydrolysis of one chlorine radical.

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Electromotive force titrations, using the hydrogen electrode, were tried, but without success. It was found that the cobaltammine solutions lost their color after standing a few hours in contact with the platinized electrode when a current of hydrogen was passing through the solution. When the electrode was removed, or when the current of hydrogen was turned off, this reduction did not take place. This indicated that the reduction was caused by the hydrogen dissolved in, or adsorbed upon, the finely divided platinum. This suggested interesting electromotive force experiments, but the method was evidently unsuited for our purpose. The oxygen electrode was also tried but no constant readings were obtained.

Titrations by means of electrical conductivity measurements were then resorted to, with more success. The solutions after being heated for a specified length of time at a given temperature were cooled and titrated. The alkali was added from a small buret graduated to 0.01 cc. Phenolphthalein was also added to these solutions and the rather indefinit point at which the pink color became evident was noted. The bridge readings were plotted against the number of cubic centimeters of the alkali added and the point of minimum conductivity determined graphically. This could be done with considerable accuracy in all the cases recorded in the tables. The phenolphthalein end point corresponded, as nearly as could be determined, with the electrical one.

TABLE XVI.—ELECTRICAL TITRATION OF SOLUTIONS OF CHLOROPENTAMMINE COBALT CHLORIDE IN WATER.

No.	Coucentration of salt molar.	Volume of solution cm³.	Temperature of titration.	Concentration of HCl molar.	Time of heating. Hours.	Temperature of heating.	NaOH 0.1 *M* added at maximum. cm³.	Excess NaOH solution. cm³.
1	0.004100	50.00	25.0°	0	0	..	0	0
2	0.003692	100.00	25.0	0.02	0	..	19.98	—0.02
3	0.003692	100.00	25.0	0.02	0	..	19.91	—0.09
4	0.004140	50.00	25.0	0	2	60°	0.17	0.17
5	0.003996	50.00	16.5	0.02	2	60°	10.02	0.02
6	0.004140	50.00	25.0	0	2¾	60°	0.38	0.38
7	0.003996	50.00	16.5	0.02	4	60°	10.30	0.30

The results (Table XVI) show a slight *increase* in the apparent acidity of the solutions which have been heated to 60°, as compared with the unheated solutions. This indicates certainly that no decomposition took place. The slight increase (0.02 to 0.38 cc.) in apparent acidity may be due to the formation of the more largely hydrolyzed roseo salt. Although the minima in the conductivity curves obtained with these solutions in which no decomposition had taken place were fairly sharp, with solutions which were known to have undergone decomposition, the minima became very indefinit, due perhaps to the ammonium and cobalt salts formed. This method then told us when no decomposition had taken place, but was useless to measure the extent of decomposition.

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We finally resorted to the same method as was employed at 25° to measure the velocity of transformation, namely, successive measurements of the electrical conductivity. A 400 cc. flask, containing the dilute acid solution, was hung in a thermostat adjusted to the desired temperature, and when the conductivity of the acid had become constant, the salt was dropped in and the solution thoroughly mixed by means of the dip electrode. Readings were then taken at frequent intervals, until the change was complete. A liquid thermostat was used for temperatures below 100°, but a steam jacket was used for the measurements at 100°. The apparatus for this purpose consisted of an inverted bell-jar fitted with a cover from which the flask was hung. Steam was led in at the top of the bell-jar and allowed to flow out at the bottom.

The results obtained with 0.02 *M* purpureo chloride in 0.02 *N* hydrochloric acid are typical of what was observed at 100°. They are given numerically in Table XVII and graphically in Curve II, Fig. I, where the specific conductivity is plotted against the time.

TABLE XVII.—CONDUCTIVITY MEASUREMENTS SHOWING DECOMPOSITION OF A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 *N* HCl.

Time. Minutes.	Temperature. °.	Sp. conductivity 1/ohms.	Remarks.
11	96.4	0.02627	
15	98.9	0.02651	
19	99.6	0.02636	
23	99.6	0.02611	
27	99.6	0.02585	
31	99.6	0.02566	
35	99.6	0.02537	
39	99.6	0.02510	
43	99.6	0.02484	
48	99.6	0.02461	
53	99.6	0.02432	
57	99.6	0.02407	
61	99.6	0.02384	
65	99.6	0.02359	
69	99.6	0.02330	
73	99.6	0.02305	
77	99.6	0.02280	
81	99.6	0.02254	
86	99.6	0.02222	
87	99.6	0.02200	
89	99.6	0.02177	
91	99.6	0.02153	Black oxide of cobalt precipitated here.
93	99.6	0.02125	
95	99.6	0.02143	
96	99.7	0.02254	
97	99.7	0.02401	

It will be observed that the conductivity first rizes, then falls at a fairly constant rate, only to rize again very sharply indeed. The beginning

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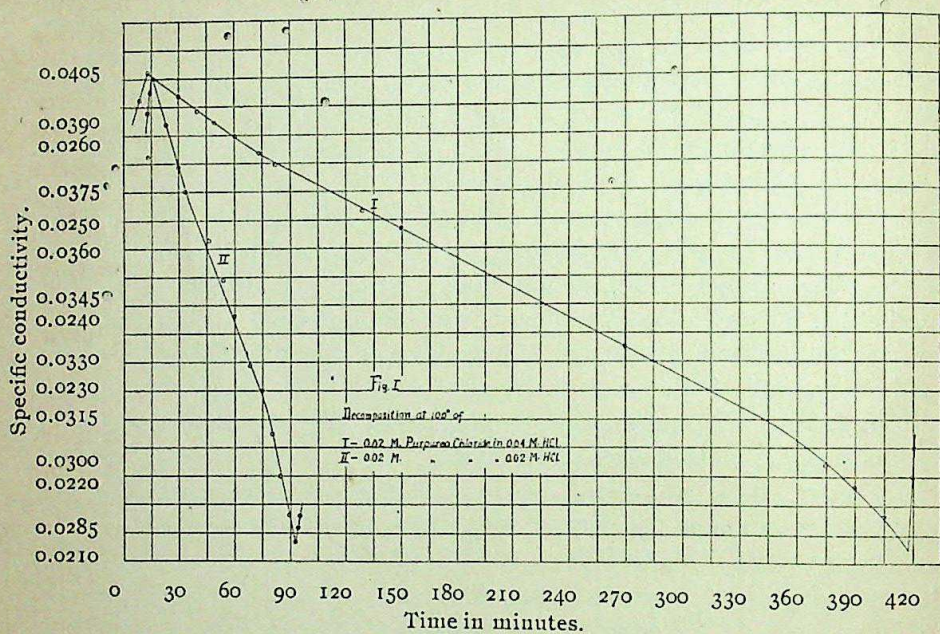
of the last very sharp rize always just precedes the separation of the black oxide of cobalt from the solution. It is evident that the initial rize of



the curve is due largely to the fact that the solution is somewhat cooled by the introduction of the salt; doubtless it is partly due to the formation of the roseo modification and the consequent increase in the number of ions. Decomposition, however, has been going on steadily, setting free ammonia, and this has decreased the original acidity, and hence by the removal of the swiftly moving hydrogen ions has decreased the conductivity. This decomposition soon becomes the dominating factor, increasing slightly in its velocity as the solution becomes less and less acidic. Finally, as the neutral point is reached, the decomposition becomes much more rapid, and since now the rapidly moving hydrogen ions are practically all removed, further decomposition, involving the liberation of rapidly moving hydroxyl ions, increases rather than decreases the conductivity. Moreover, the cobalt hydroxide, one of the products of decomposition, would appear as soon as the neutral point is passed.

The approximately linear course of the main portion of the curve is not without interest. It indicates that the rate of decomposition is approximately constant over a fairly long-time interval. There are evidently two influences at work: the concentration of the cobaltammine is steadily decreasing, which would tend to diminish the rate, and the acid concentration is also decreasing, which would increase the rate. The change in concentration of the cobaltammine is relatively slight, in the case studied, up to the neutral point; the acidity at first decreases slowly, but as the

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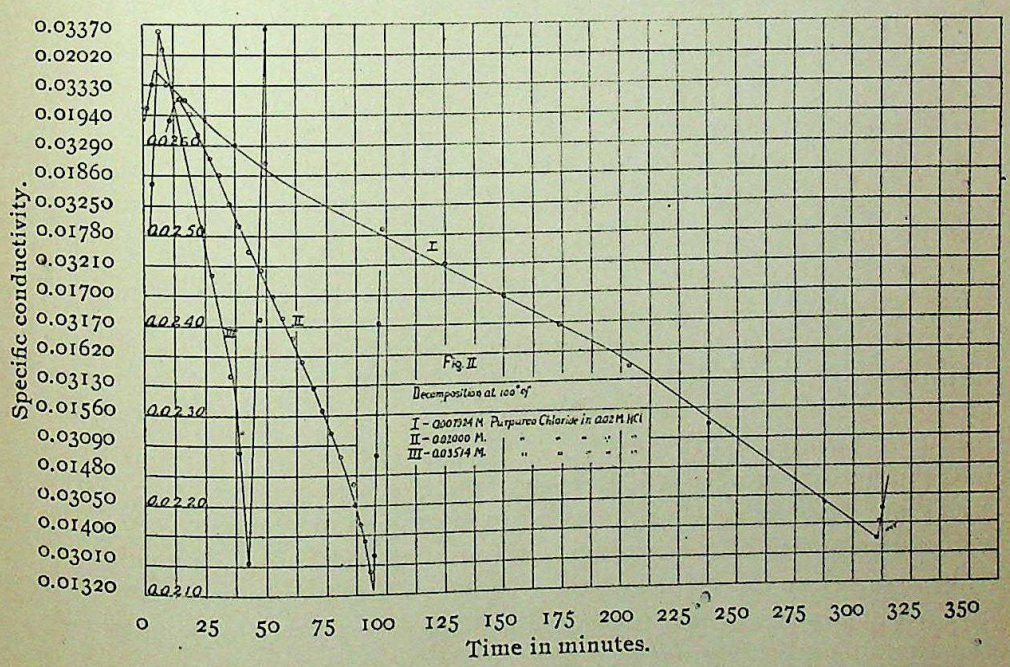
neutral point is reached very rapidly indeed. In fairly acid solutions then, we should expect a very nearly straight curve, but as the neutral point is reached this should drop very rapidly indeed, only to rize still more rapidly when the neutral point is passed. It will be seen that this is actually the case.

Fiftieth molecular purpureo chloride in twenty-fifth normal hydrochloric acid gives the same form of curve (Curve I, Fig. I) but the time interval is longer. A doubling of the concentration of the acid lengthens by more than four times the time required to reach neutrality. It should lengthen it but twice, assuming an approximately linear decomposition curve and no specific effect of acid on the rate. This confirms our previous conclusion that acid does slightly lessen the rate of decomposition.

The effect of a change in the concentration of the purpureo chloride, keeping the acid concentration the same, was tried. 0.007924 and a 0.03514 molar solutions of chloropentammine cobalt chloride were heated to 99.4° in 0.02 molar hydrochloric acid. Their change in conductivity with the time is given in Curves I and III of Fig. II. From this figure



one sees that the most concentrated solution evidently reaches the neutral point much sooner. This would be expected, for the more concentrated the cobaltammine the more rapidly it should decompose. If the rate of this decomposition were directly proportional to the concentration of the cobaltammine and was nevertheless kept nearly constant in each case by the decreasing concentration of the acid, since the solu-

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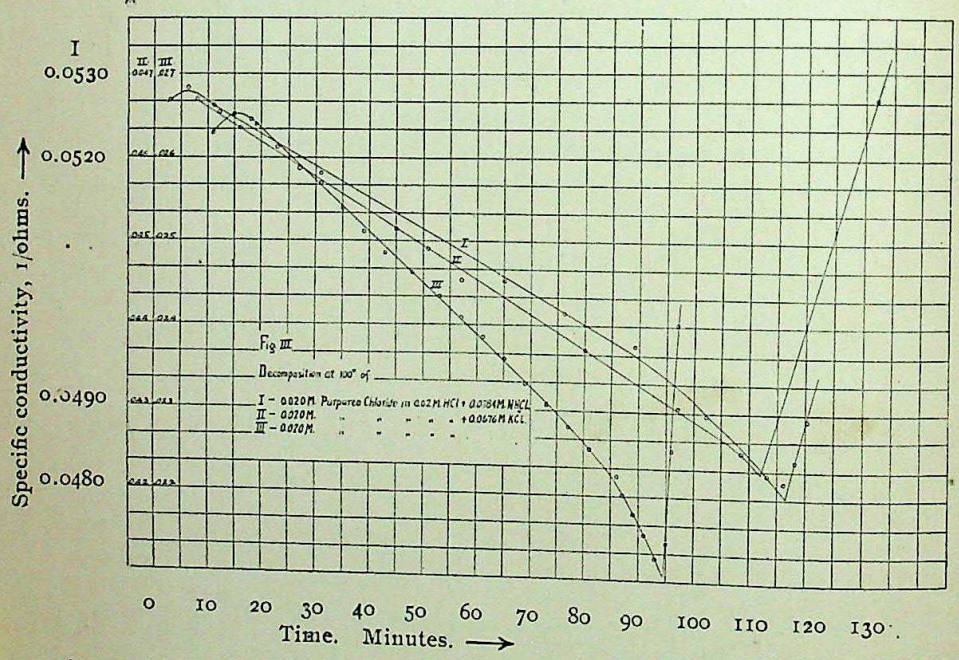
tion represented by Curve III is about five times as concentrated as that represented by Curve I, we should expect that the concentrated solution would reach the neutral point in about one-fifth the time of the more dilute, or in about sixty-five minutes. It actually reaches this point in about forty-five minutes.

It was also of interest to determin the effect on the rate of decomposition of an increase in the concentration of the chlorine ion without any change in the acid concentration. Potassium chloride was added to the solution of the purpureo chloride in hydrochloric acid. That the rate of decomposition was but slightly affected by this change can be seen from Curves II and III of Fig. III.



A 0.02 molar solution of chloropentammine cobalt chloride in a 0.02 molar hydrochloric acid solution which contained ammonium chloride at a concentration of 0.0784 molar was also studied and its decomposition was found to follow a curve very similar to that of a potassium chloride solution of the chloropentammine. This shows that the ammonium ion exerts no specific influence.

Solutions of the nitratopentammine cobalt nitrate in dilute nitric acid decomposed so rapidly at 100° that measurements were not undertaken.

A solution of bromopentammine cobalt bromide, 0.02 molar, in 0.02 molar hydrobromic acid gave a curve very similar to that given by the chloro-chloride, and took very nearly the same time to reach neutrality (Curve III, Fig. IV).

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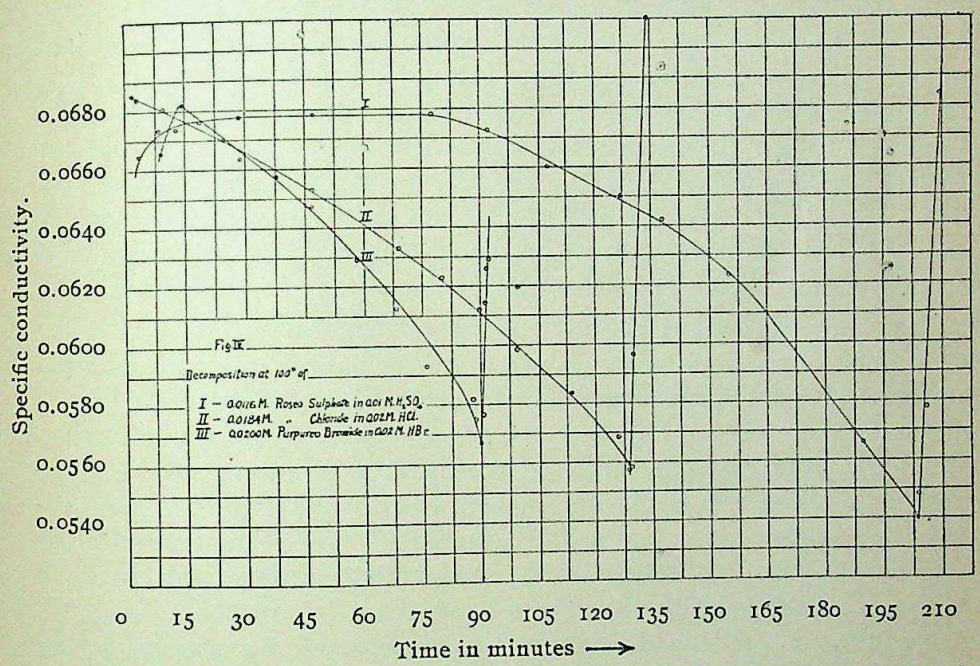
A solution of 0.01 molar aquopentammine cobalt sulfate in 0.01 molar sulfuric acid follows a slightly different form of curve (Curve I, Fig. IV). The conductivity remains nearly constant for some time, but



finally falls off at an increasing rate until neutrality is reached, when it rapidly increases. The time required to reach neutrality is considerably greater than in the case of the chloride.

A 0.0184 molar solution of aquopentammine cobalt (roseo) chloride in 0.02 molar hydrochloric acid was found to decompose in much the same fashion as the purpureo salt (chloropentammine cobalt chloride). In spite of the lowering of temperature caused by the introduction of the salt there is no initial rise in the curve, indicating that the initial rise observed with the purpureo salt was indeed due to conversion into roseo, as well as to the rise in temperature (Curve II, Fig. IV). The roseo chloride reaches neutrality more slowly than the corresponding purpureo chloride, but this is partly due to the greater dilution of the roseo chloride solution. When the time intervals required by the various purpureo chloride solutions to reach neutrality in 0.02 molar hydrochloric acid are plotted against the concentrations of these solutions and the connecting curve is drawn, it is found that the corresponding time interval for the roseo chloride solution still lies, however, somewhat above this curve, indicating a somewhat slower decomposition even when corrected for the difference of concentration.

Experiments were also undertaken to determin the effect of ammonia

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on the rate of decomposition; that is, to find whether, if the ammonia were not allowed to escape from the solution after the neutral point was passed, the rate of decomposition would be increased or decreased. First, using small bottles with loosely fitting stoppers, it was found that the 0.02 molar solution of the purpureo chloride in 0.02 molar hydrochloric acid, which, under the above conditions, required about 95 minutes for the appearance of the cobalt oxide, now required in three separate experiments 132–135 minutes. When the same solution was employed, but the whole was sealed in a thick-walled glass tube, the time was lengthened to 201 minutes. This shows that once the neutral point is passed the presence of ammonia lessens the rate of decomposition. This appears reasonable from what we know of the methods of formation of the cobaltammines.

Gaseous Products of the Decomposition.

Bubbles of gas were given off within a few moments after the salt was dropped into the various solutions at 100°. This indicated that aside from the mere decomposition of the cobaltammine, there was also a reduction of the trivalent cobalt to the divalent condition, with a corresponding liberation either of oxygen, or of nitrogen derived as a secondary product from the oxidation of the ammonia. We therefore undertook experiments, first to determin the amount and nature of this gas, and secondly to determin the extent of the reduction.

To determin the amount of the gas a simple apparatus was employed, consisting chiefly of a flask whose volume was 350 cc. when completely filled. The neck of the flask was closed with a stopper whose lower surface had been hollowed out and provided with a capillary outlet tube which could be closed by a stopcock. All bubbles of gas which rose to the top of the liquid made their way easily into this outlet tube. Another outlet tube was sealed into the neck sloping very obliquely downward from the neck, and this in turn was sealed to a vertical U-tube. This U-tube had a volume of fifty cc. and was partly filled with mercury. This arrangement provided for any change in volume of the liquid contained in the closed flask. A thermometer was also fitted into the flask through a hole in the rubber stopper. The flask was first filled nearly full with the acid solution, and heated for some time in a steam bath to 100°, the salt was then dropped in, the stopper inserted, and by blowing on the outer branch of the U-tube the level of the solution was raised in the flask and then all the air forced out. By a suitable arrangement of the stopcocks the gas, as fast as it was formed in the decomposition flask, was similarly forced over into the gas pipet containing acid, and all the ammonia absorbed. Very little gas was given off after the black oxide of cobalt had precipitated and the runs were therefore stopped at that point. This gas was then carefully measured over water in a small buret graduated to 0.02 cc. It was then passed into an alkaline pyro-

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gallol solution and again measured. The residual gas was shown to be nitrogen by adding hydrogen and sparking over sulfuric acid. The decrease in volume corresponded very nearly, after twenty-four hours, to four times the original volume. The volumes of gas found are given in Table XVIII.

TABLE XVIII.—VOLUME AND COMPOSITION OF GAS[1] GIVEN OFF ON HEATING A SOLUTION OF 1.75 GRAMS CHLOROPENTAMMINE COBALT CHLORIDE IN 350 CC. 0.02 MOLAR HYDROCHLORIC ACID. TEMPERATURE 20°.

No.	Time of decomposition. Minutes.	Temperature. °.	Barometric pressure. Mm. Hg.	Volume gas. Total Cc.	Volume N_2. Cc.	Volume O_2. Cc.	Equivalent volume O_2. Cc.
1....	106	99.45	756.4	5.06	4.52	0.54	7.32
2....	106	99.38	757.2	5.10	4.60	0.50	7.40
3....	104	99.45	757.1	4.99	4.44	0.55	7.22
							7.31

Calculated equivalent volume of oxygen if complete reduction had taken place = 42.9 cc.

These experiments showed that both oxygen and nitrogen were given off, but in amounts corresponding to only about one-fifth of the total salt present, assuming complete reduction.

The Determination of Trivalent Cobalt.

Either reduction was not complete in these experiments, or some non-gaseous oxidation product was formed. A method was therefore worked out for determining the amount of unreduced *i. e.*, trivalent cobalt present at any time. It was found namely that the purpureo chloride was completely decomposed by boiling for an hour and a half with hydriodic acid under definit conditions. 0.5 gram of the purpureo chloride was boiled with a solution of 1.5 cc. sulfuric acid and 5 grams of potassium iodide in 100 cc. of water in a small flask provided with a reflux condenser. To the end of the condenser were attached in series two absorption bulbs containing concentrated solutions of potassium iodide. An inlet tube, reaching below the surface of the liquid in the flask was also provided and through this was passed a current of purified carbon dioxide gas. Indeed, the whole apparatus was filled with this gas before heating was begun. The iodide liberated was carried over by the current of gas; the second absorption bulbs were never more than faintly yellow, showing that the absorption was complete. The whole apparatus was of glass. The iodine was titrated by means of a sodium thiosulfate solution. Blank tests were run without the addition of any salt; 0.50 cc. and 0.60 cc., respectively, of the thiosulfate solutions were required. This slight amount of iodine was perhaps formed by the traces of oxygen still present in the solution and in the apparatus or as iodate in the iodide.

[1] We wish to thank Mr. John F. W. Schulze for his careful execution of these experiments on the gaseous products of decomposition.

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Two analyses of pure purpureo chloride were then made (0.4983 and 0.5040 gram) requiring, respectively, 20.15 cc. and 21.00 cc. of the sodium thiosulfate solution. The calculated volumes, taking the blank tests into account, were 20.00 cc. and 21.05 cc. respectively. This agreement is within the experimental error.

This method was now employed to follow the reduction of a purpureo chloride solution at 100°. 0.5000 gram of the purpureo chloride was added to 100 cc. of 0.02 molar hydrochloric acid previously warmed to 100°; this was kept in a steam bath for a specified length of time, then cooled. 5 grams of potassium iodide and 1.5 cc. of sulfuric acid were added. The air was then expelled from the apparatus by means of carbon dioxide and the analysis completed as before. In this way the purpureo chloride was decomposed under exactly the same conditions as in previous experiments, and at the same time the analytical conditions were not altered. The results are given in Table XIX.

TABLE XIX.—RATE OF REDUCTION OF A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 HYDROCHLORIC ACID, AT 100°, MEASURED ANALYTICALLY.

No.	Time of heating. Minutes.	$Na_2S_2O_3$ required. Cc.	$Na_2S_2O_3$ corrected. Cc.	Percentage reduction.	Remarks.
1	25	18.70	18.15	10.6	
2	50	18.30	17.75	12.6	
3	77	16.60	16.05	20.9	The oxide of cobalt was precipitated only in No. 5
4	90	15.55	15.00	26.1	
5	105	15.50	14.95	26.4	

The Composition of the Black Oxide of Cobalt.

Two samples of the black oxide of cobalt were then prepared by the decomposition of a 0.02 molar solution of purpureo chloride in 0.02 molar hydrochloric acid. They were washed for a long time by decantation, as filtration proved impracticable, and then dried by standing over sulfuric acid. The results are given in Table XX.

TABLE XX.—ANALYSIS OF BLACK OXIDE.

No.	Oxide taken. Gram.	$Na_2S_2O_3$ solution required. Observed. Cc.	$Na_2S_2O_3$ solution required. Corrected. Cc.	$Na_2S_2O_3$ solution calculated Co_2O_3. Cc.	$Na_2S_2O_3$ solution calculated Co_2O_4. Cc.	Percentage reduction.
1	0.2360	19.80	19.25	29.43	20.15	34.59
2	0.1992	16.70	16.15	24.70	17.14	34.62

These analyses confirm our conclusion that the cobalt is only partially reduced during this decomposition. If we consider that the oxide still contained, in all probability, traces of water, the analytical values agree excellently with the requirements of the formula Co_3O_4. This is in exact agreement with the supposition of Gibbs[1] that from a neutral solution

[1] *Loc. cit.*

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of purpureo chloride on boiling, "a dark brown precipitate, probably of the hydrated magnetic oxide, is thrown down."

All these experiments on the decomposition of purpureo chloride indicate that the decomposition of the ammine progresses nearly to completion with only a partial reduction of the cobalt. The gas experiments gave a somewhat smaller percentage reduction than the digestion experiments with hydriodic acid; this would indicate that some gaseous oxidation products are formed in solution which are reduced by the hydriodic acid.

Velocity of Decomposition.

In any case, it was evident that the decomposition at 100° was altogether too rapid to permit of equilibrium experiments at that temperature. The rate of decomposition and transformation at lower temperatures were therefore investigated (Tables XXI, XXII and XXIII).

TABLE XXI.—CONDUCTIVITY MEASUREMENTS SHOWING RATE OF DECOMPOSITION OF A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 60°.

Time. Hours.	Temperature. °.	Specific conductivity 1/ohms.
0	60.0	0.01360
0.3	60.0	0.01923
1.9	60.0	0.02032
9.5	60.0	0.02175
26.1	60.0	0.02315
46.1	60.0	0.02315
57.2	60.0	0.02454
72.1	60.0	0.02418
93.9	60.0	0.02301
117.7	60.0	0.02244
143.2	60.0	0.02224

TABLE XXII.—CONDUCTIVITY MEASUREMENTS SHOWING RATE OF DECOMPOSITION OF A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 70°.

Time Hours.	Temperature. °.	Specific conductivity 1/ohms.
0	70.0	0.01414
0.05	70.0	0.02115
0.3	70.0	0.02311
12.3	70.0	0.02499
13.4	70.0	0.02520
15.5	70.0	0.02525
17.7	70.0	0.02525
24.7	70.0	0.02520
31.2	70.0	0.02505
50.7	70.0	0.02468

Complete decomposition only after eleven days.

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TABLE XXIII.—CONDUCTIVITY MEASUREMENTS SHOWING RATE OF DECOMPOSITION OF A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 75°.

Time. Hours.	Temperature. °.	Specific conductivity 1/ohms.
0	75.0	0.01454
0.05	75.0	0.02259
0.17	75.0	0.02330
0.35	75.0	0.02408
9.1	75.0	0.02753
10.2	75.0	0.02746
11.5	75.0	0.02639
13.8	75.0	0.02617
20.5	75.0	0.02573
33.5	75.0	0.02463

These results show that the maximum conductivity, that is, complete conversion into roseo, is not attained at 60° until after some sixty hours, at 70° until after thirteen hours and at 75° until after something less than nine hours. The subsequent decrease in conductivity, that is, the decomposition, is very slow at both 60° and 70°, requiring at 70° some ten or twelve hours to become perceptible. On the other hand, at 75° the rate of decomposition is decidedly more rapid, producing a noticeable change in conductivity within an hour. These results evidently agree with those obtained by the electrical titration measurements. 70° is evidently the optimum temperature for equilibrium measurements.

Measurements on the Roseo-Purpureo Chloride Equilibrium.

We now took up the study of the equilibrium between the purpureo and roseo compounds under these optimum conditions, that is, at 70° and in weakly acid solution. The most suitable method for this purpose in the case of the chloride appeared to be the determination of the precipitable and unprecipitable chlorine in the mixture. This could evidently be accomplished by adding an excess of silver nitrate to the mixture, filtering, converting the purpureo salt in the filtrate into roseo by adding ammonia, boiling, acidifying and again filtering from the precipitated silver chloride. The weight of either precipitate, compared with the total precipitate or the weight of salt taken, tells us the per cent. of roseo salt in the mixture. Since, however, from our conductivity experiments, we know that the transformation takes place with some rapidity at 70°, it was necessary to cool the equilibrium mixture rapidly to room temperature, or lower, before the precipitation, to prevent a shifting of the equilibrium. Even at these lower temperatures we know that a slow transformation takes place and consequently the filtration of the silver chloride must be rapid.

The method of procedure finally adopted to meet these requirements was as follows: 100 cc. of standardized hydrochloric acid solution were

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measured into Jena glass flasks of that capacity. They were then placed in the thermostat at 70° and when they had reached this temperature, a weighed quantity of salt, usually about 0.5 gram, was added. This dissolved rapidly to a clear, dark-red solution. After given intervals of time the flasks were removed and their contents quickly poured over a mixture of ice and water in Erlenmeyer flasks. A few drops of nitric acid and an excess of silver nitrate were then added, the flasks closed with their ground-in stoppers and shaken. The clear, supernatant liquid was now filtered off rapidly by suction through a porous alundum crucible and transferred to a 600 cc. Erlenmeyer flask, a slight excess of ammonia added and the whole boiled until the conversion into roseo salt was complete. The solution was then acidified and the precipitated silver chloride collected in a platinum Gooch crucible, and heated to constant weight in an electric oven at 140°.

We first carried through a preliminary series of analyses to get a rough idea of the location of the equilibrium. In these experiments both the first and second precipitate of silver chloride were weighed. The results are given in Table XXIV.

TABLE XXIV.—PRELIMINARY MEASUREMENTS OF THE EQUILIBRIUM IN A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN A 0.02 MOLAR HYDROCHLORIC ACID SOLUTION AT 70°.

No.	Wt. purpureo.	Time of heating. Hrs.	Wt. 1st ppt. AgCl from HCl and purpureo.	Wt. AgCl from HCl.	Wt. 1st ppt. AgCl from purpureo.	Wt. 2nd ppt. AgCl.	Total wt. AgCl.	Total wt. AgCl calc.	% roseo calc. from wt. 1st ppt.	% roseo calc. from wt. 2nd ppt.
1	0.5000	1	1.0060	0.2818	0.7242	0.1350	0.8592	0.8600	52.30	52.88
2	0.5000	5.5	1.0548	0.2818	0.7730	0.0862	0.8592	0.8600	68.95	66.53
3	0.5000	17	1.0597	0.2818	0.7779	0.0808	0.8587	0.8600	71.00	71.25
4	0.5000	23	1.0621	0.2818	0.7803	0.0780	0.8583	0.8600	71.74	72.74
5	0.5000	27	1.0698	0.2818	0.7880	0.0716	0.8596	0.8600	75.00	75.10

These preliminary experiments showed a rapid increase in the percentage of roseo salt up to seventeen hours and a very slow increase thereafter, and indicated that in this solution at equilibrium there was approximately 71 per cent. of roseo salt present. The agreement between the weight of the first and the second precipitate of silver chloride establishes the reliability of both methods of analysis; in the following experiments therefore we have only weighed the second precipitate.

It was first necessary to show that the cooling was sufficiently rapid to prevent a shifting of the equilibrium before a low temperature had been reached. For this purpose we carried out a series of experiments identical in every respect among themselves except in the rate of cooling. This difference in the rate of cooling was obtained by using different relative amounts of ice and distilled water in the Erlenmeyer flasks into which the equilibrium mixtures were poured. The results of these experiments are given in Table XXV.

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TABLE XXV.—EFFECT OF DIFFERENT RATES OF COOLING ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID.

No.	Weight purpureo. Gram.	Rate of cooling.	Weight AgCl. Gram.	Per cent. roseo.	Remarks.
6	0.5000	Cooled very slowly. Filtered after 1 hour.	0.0636	77.84	Silver nitrate and nitric acid added to the ice-water.
7	0.5000	Cooled slowly. Filtered after ½ hour.	0.0702	75.54	Silver nitrate and nitric acid added one minute after pouring equilibrium mixture.
8	0.5000	Cooled more rapidly	0.0788	72.54	
9	0.5000	15 sec. 40° 30 sec. 40° 60 sec. 40°	0.0822	71.29	
10	0.5000	15 sec. 23° 30 sec. 21° 60 sec. 20.9°	0.0854	70.25	
11	0.5000	15 sec. 9° 30 sec. 3.5° 60 sec. 2°	0.0858	70.10	
12	0.5000	15 sec. 2° 30 sec. 2° 60 sec. 1°	0.0865	69.86	

It will be seen from these results that slow cooling has a decided effect on the equilibrium, but that in the three experiments with the most rapid cooling the difference is not greater than the experimental error. In our further analyses we therefore cooled as in No. 12, added the precipitant at the end of one minute, shook and filtered immediately.

We now repeated our preliminary equilibrium measurements using these precautions as to cooling and obtained the results given in Table XXVI.

TABLE XXVI.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight salt. Gram.	Time of heating. Hours.	Weight second precipitate AgCl. Gram.	Per cent. roseo.
13	0.5000	...	0.2685	6.62
14	0.5000	0.90	0.1228	57.21
15	0.5000	3.03	0.0862	69.97
16	0.5000	6.55	0.0858	70.14
17	0.6000	17.72	0.0851	70.35
18	0.5000	24.72	0.0850	70.38
19	0.5000	27.60	0.0821	71.39

These experiments agree excellently with experiments Nos. 10, 11 and 12. As would be expected, they give results somewhat lower than the more slowly cooled experiments Nos. 3 and 4.

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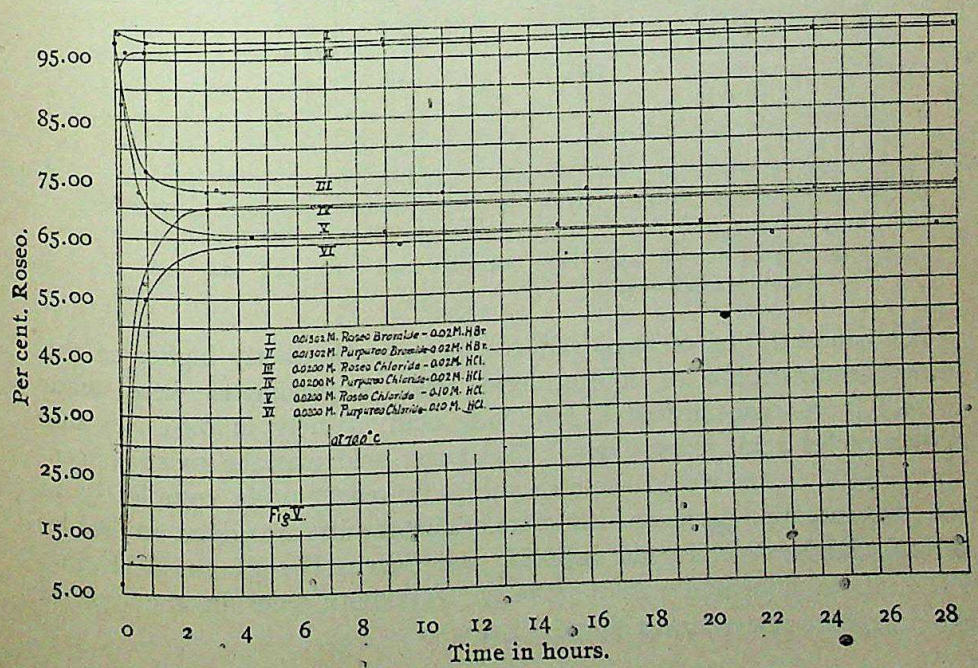
The next logical step was to find whether or not this was a true equilibrium. This was done by starting with the roseo instead of the purpureo salt in a solution of the same molecular concentrations. The results are recorded in Table XXVII.

TABLE XXVII.—EQUILIBRIUM MEASUREMENTS ON 0.02 MOLAR SOLUTION OF PENTAMMINE COBALT CHLORIDE (ROSEO) IN 0.02 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
20	0.5360	...	0.0082	97.64
21	0.5360	0.97	0.0682	76.24
22	0.5360	3.33	0.0770	73.14
23	0.5360	11.0	0.0798	72.29
24	0.5360	16.0	0.0802	71.99
25	0.5360	24.0	0.0840	70.78

These results are plotted against the time in Fig. V, Curves III and IV. It is seen that the two curves come very nearly together. The slight difference between the two curves is probably only apparent; it may be due to a trace of moisture present in the roseo salt. This experiment demonstrates that a real equilibrium exists in these solutions between the roseo and the purpureo salts. Further proof of this will also be found in the experiments on 0.02 molar purpureo and roseo chloride in 0.10 molar hydrochloric acid and in the experiments on 0.01302 molar roseo and purpureo bromide in 0.02 molar hydrobromic acid (see Curves I, II, V and VI in Fig. V).



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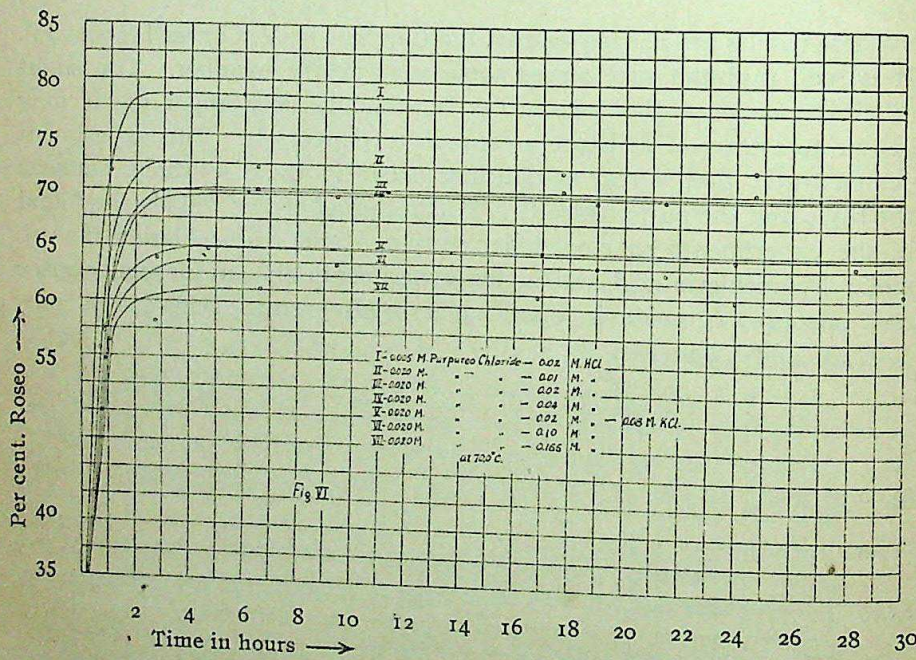
Similar experiments were now made on the equilibrium in a 0.02 molar solution of purpureo chloride in 0.01 molar hydrochloric acid. The results are given in Table XXVIII, Curve II, Fig. VI.

TABLE XXVIII.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.01 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight of salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
26	0.5000	0.78	0.1275	55.58
27	0.5000	3.03	0.0793	72.37
28	0.5000	6.55	0.0799	72.17
29	0.5000	17.72	0.0802	72.07
30	0.5000	24.72	0.0792	72.40
31	0.5000	30.0	0.0791	72.43



The concentration of roseo salt is seen to be distinctly higher at this lower concentration of hydrochloric acid. Experiments were made in still more concentrated hydrochloric acid; namely in 0.04, 0.1 and 0.1660 molar acid, respectively. This latter acid was the most concentrated acid which would dissolve the purpureo chloride completely at the concentration used (0.02 molar). The results are given in Tables XXIX, XXX, XXXI, and XXXII, and Curves IV, VI and VII, Fig. VI. The equilibrium was approached from both sides in the case of the 0.1 molar acid (Curves V and VI, Fig. V).

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TABLE XXIX.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.04 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
32	0.5000	0.78	0.1431	50.00
33	0.5000	3.97	0.0938	67.30
34	0.5000	9.47	0.0871	69.65
35	0.5000	19.0	0.0878	69.41
36	0.5000	21.47	0.0870	69.67
37	0.5000	27.0	0.0855	70.19

TABLE XXX.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF AQUOPENTAMMINE COBALT CHLORIDE (ROSEO) IN 0.10 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight roseo. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
20	0.5360	0	0.0082	97.64
38	0.5360	0.75	0.0785	72.63
39	0.5360	3 (?)	0.0811	71.72
40	0.5360	9	0.0985	65.69
41	0.5360	15	0.0978	65.94
42	0.5360	20	0.0986	65.62

TABLE XXXI.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.10 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
43	0.5000	0.93	0.1302	54.63
44	0.5000	4.0	0.1043	63.66
45	0.5000	9.50	0.1050	63.41
46	0.5000	19.0	0.1043	63.66
47	0.5000	21.5	0.1056	63.20
48	0.5000	28.28	0.1030	64.11

TABLE XXXII.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.166 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
49	0.5000	1.08	0.1252	56.38
50	0.5000	2.78	0.1201	58.16
51	0.5000	6.69	0.1117	61.08
52	0.5000	16.85	0.1120	60.98
53	0.5000	24.0	0.1120	60.98
54	0.5000	30.0	0.1100	61.67

These experiments show clearly that the percentage of roseo salt, and hence its concentration, decreases steadily as the concentration of the hydrochloric acid is increased. To determin whether this was due to the hydrogen ion or the chlorine ion an experiment was carried out with

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a 0.02 molar solution of the purpureo salt in 0.02 molar hydrochloric acid to which enough potassium chloride was added to bring the concentration of the chlorine ions up to approximately 0.1 normal. The results are given in Table XXXIII, and in Curve V, Fig. VI.

TABLE XXXIII.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID PLUS 0.08 MOLAR POTASSIUM CHLORIDE SOLUTION AT 70°.

No.	Weight of purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
55	0.5000	0.92	0.1207	57.64
56	0.5000	2.84	0.1036	63.90
57	0.5000	4.75	0.1012	64.74
58	0.5000	17.0	0.1007	64.91
59	0.5000	24.0	0.1019	64.48

This experiment shows that the equilibrium concentration of the roseo salt in this solution is identical with that in a 0.1 molar solution of hydrochloric acid. This demonstrates that it is the concentration of the chlorine ion and not of the hydrogen ion which affects the equilibrium. This is what would be expected from the equation already given for the change.

The effect of a change in the concentration of the ammine itself was then tried. 0.005 and 0.05361 molar solutions of the purpureo salt in 0.02 molar hydrochloric acid were taken. The results are given in Tables XXXIV and XXXV, and in Curve I, Fig. VI.

TABLE XXXIV.—EQUILIBRIUM MEASUREMENTS ON A 0.005 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 70°. (A 400 CC. SAMPLE INSTEAD OF A 100 CC. SAMPLE WAS TAKEN.)

No.	Weight of purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
60	0.5000	1.08	0.0956	71.69
61	0.5000	3.25	0.0616	78.54
62	0.5000	6.0	0.0616	78.54
63	0.5000	18.0	0.0622	78.30
64	0.5000	30.0	0.0630	78.05

TABLE XXXV.—EQUILIBRIUM MEASUREMENTS ON A 0.05361 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight purpureo salt Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
65	0.6713	14.1	0.1291	66.38
66	0.6713	17.3	0.1289	66.44
67	0.6713	22.7	0.1292	66.35

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These experiments show the more dilute the solution of the cobaltammine the greater the percentage of roseo salt at the equilibrium. This agrees with our previous inferences stated at the outset of the paper.

Just the opposit shifting of the equilibrium took place when ammonium nitrate instead of the chloride was added to the solution. To a solution of fiftieth molar hydrochloric acid ammonium nitrate was added in sufficient quantity to make a tenth-normal solution. It will be seen from Table XXXVI that the results was a large increase in the percentage of roseo salt present at equilibrium. This would indicate that some nitratopentammine salt is formed, which is, of course, equivalent to a decrease in the total concentration of the chloropentammine salt plus the roseo pentammine salts; we have just seen that such a decrease in concentration results in a greater relative concentration of the roseo salt at equilibrium. There is then no evidence of any specific effect of the ammonium ion.

TABLE XXXVI.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN A SOLUTION 0.02 MOLAR WITH RESPECT TO HYDROCHLORIC ACID AND 0.1 MOLAR WITH RESPECT TO AMMONIUM NITRATE.

No.	Weight of purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13.....	0.5000	0	0.2685	6.62
68.....	0.5000	1.08	0.0947	67.00
69.....	0.5000	3.17	0.0589	79.48
70.....	0.5000	19.0	0.0595	79.27
71.....	0.5000	20.0	0.0601	79.10
72.....	0.5000	27.0	0.0600	79.07

The measurements on the purpureo-roseo chloride equilibrium are collected in Table XXXVII.

TABLE XXXVII.—SUMMARY OF MEASUREMENTS ON PURPUREO-ROSEO COBALT CHLORIDE EQUILIBRIUM AT 70°.

No. Equilibrium.	Concentration molar. Total ammine.	HCl.	Roseo. Per cent.	Purpureo. Per cent.	Concentration molar. Roseo. Total.	Purpureo. Total.	Roseo ion.	Purpureo ion.	Chlorine ion.
1	0.02	0.01	72.3	27.7	0.01446	0.00554	0.00940	0.00387	0.0449
2	0.02	0.02	70.8	29.2	0.01416	0.00581	0.00888	0.00401	0.0531
3	0.02	0.04	69.7	30.3	0.01394	0.00606	0.00832	0.00398	0.0694
4	0.02	0.10	63.7	36.3	0.01274	0.00726	0.00677	0.00430	0.1182
5	0.02	0.166	61.0	39.0	0.01220	0.00780	0.00591	0.00422	0.1716
6	0.005	0.02	78.5	21.5	0.003925	0.001075	0.00271	0.000804	0.02844
7	0.05361	0.02	66.4	33.6	0.03560	0.01801	0.01963	0.01103	0.0989
8	0.02	0.02+0.08 KCl	64.8	35.2	0.01296	0.00704	0.00686	0.00414	0.1181

The Equilibrium Constant.

Our analytical results only tell us the total concentration of roseo and of purpureo compounds in the equilibrium mixtures. Both of these sub-

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stances are certainly present in a dissociated as well as an undissociated condition, and any one or more of these individual molecular species may be the direct factor in the equilibrium. There is the further uncertainty that while the transformation of purpureo to roseo is almost certainly an intramolecular rearrangement, that of the roseo to purpureo may be either an intramolecular rearrangement of the undissociated or partially dissociated roseo salt, or it may be a direct combination of the wholly or partially dissociated roseo salt with the chlorine ion.

To determin which of these alternative possibilities actually exists, evidently requires, in addition to the above analytical data, information regarding the degree of dissociation of the substances present in the equilibrium mixtures at 70°. In the case of hydrochloric acid we have for this purpose the adequate and excellent conductivity data of A. A. Noyes and his colleagues. The only pertinent information regarding the two ammines is found in two dilution experiments of Werner and Miolati[1] on the purpureo chloride and the roseo bromide. We applied the method of Noyes[2] to these results and obtained for the roseo bromide a constant value of 1.52 for the exponent n, in excellent agreement with the values found by Noyes and Johnson[3] for salts of the same type. The data for the purpureo chloride gave no satisfactory value of n, apparently because of the inaccuracy produced by the steady transformation of purpureo into roseo salt. In view of the general similarity found by Noyes and his colleagues between salts of the same type and of the agreement of the roseo with these salts, we have simply taken the accurate measurements of Noyes and Johnston on barium and lanthanum nitrates and used them to calculate the dissociation of the purpureo and roseo chloride respectively in the various mixtures. To do this we have recalculated the values n and K for these two salts at 50°, 75°, 100°, and by interpolation have found the value of these parameters at 70°. We have carried out the same calculation for hydrochloric acid using the measurements of Noyes and Cooper.[4] The resulting expressions were as follows:

for the roseo chloride $C_{R^{+++}}^{1.49}/R_{RCl_3} = 0.375$;

for the purpureo chloride $C_{P^{++}}^{1.52}/C_{PCl_2} = 0.471$;

for the hydrochloric acid $C_{H^{+}}^{1.40}/C_{HCl} = 3.51$;

all at 70°.

We now solved all of the three equations for each mixture by a process of successive approximation making the assumption that the per-

[1] *Z. physik. Chem.*, 12, 35 (1893) and 14, 520 (1894).
[2] *Carnegie Institution Publication*, 63, p. 50.
[3] THIS JOURNAL, 31, 987–1010 (1909).
[4] *Carnegie Institution Publication*, 63, 115–149.

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centage dissociation of each substance in the mixture was the same as it would have been alone at an equivalent ionic concentration equal to the sum of the equivalent ion concentrations of the three substances present.[1]

The resulting values for the concentrations of the various ions and undissociated molecules are given in Table XXXVII. This assumption of Arrhenius is evidently equivalent to the statement that the percentage dissociation is the same in the mixtures as in pure solutions containing the same concentration of free electricity. As a variation of this we tried the assumption that the percentage dissociation of each substance would be the same in the mixture as when alone at a total *molar* ionic concentration equal to the total molar ionic concentration of the mixture. The resulting values were nearly identical with those obtained on the original assumption.

The simplest assumptions regarding the nature of the equilibrium are that it is determined solely either by (1) the total concentrations of the roseo and purpureo compounds, or (2) the concentrations of the roseo and purpureo ions or (3) the concentrations of the undissociated roseo and purpureo molecules. In each of these cases one of the following equations would apply:

$$\text{For (1)} \quad C_R/C_P = K_1,$$
$$\text{For (2)} \quad C_{R^{+++}}/C_{P^{++}} = K_2,$$
$$\text{For (3)} \quad C_{RCl_3}/C_{PCl_2} = K_3,$$

where C_R and C_P represent the total concentrations of roseo and purpureo compounds, $C_{R^{+++}}$ and $C_{P^{++}}$ the concentrations of the corresponding ions, C_{RCl_3} and C_{PCl_2} of the corresponding undissociated molecules and K_1, K_2 and K_3 equilibrium constants. A brief inspection of the calculated values of these constants as given in Table XXXVIII shows that no one of these equations is adhered to, the values of each K varying two or three times.

TABLE XXXVIII.—VALUES OF EQUILIBRIUM CONSTANT FOR PURPUREO ROSEO COBALT CHLORIDE EQUILIBRIUM AT 70° CALCULATED ON VARIOUS ASSUMPTIONS.

No.	K_1.	K_2.	K_3.	K_4.	K_5.	K_6.	K_7.
1	2.61	2.43	3.03	0.117	0.109	0.86	0.63
2	2.44	2.21	2.94	0.129	0.117	0.90	0.63
3	2.30	2.09	2.70	0.159	0.145	1.04	0.67
4	1.76	1.57	2.02	0.208	0.186	1.20	0.66
5	1.56	1.40	1.78	0.268	0.240	1.40	0.69
6	3.65	3.37	4.48	0.104	0.096	1.22	0.71
7	1.98	1.78	2.29	0.196	0.176	0.90	0.68
8	1.89	1.66	2.10	0.223	0.196	1.25	0.69
Average deviation, per cent.	21	22	23	22	26	15	3

[1] Arrhenius, *Z. physik. Chem.*, 31, 218 (1899).

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None of these simple assumptions contains an explicit expression of the chlorine ion concentration; when this is introduced, still assuming the simple concentration law, we would have

$$C_R \times C_{Cl'}/C_P = K_4$$

or

$$C_{R^{+++}} \times C_{Cl'}/C_{P^{++}} = K_5$$

where $C_{Cl'}$ represents the total concentration of the chlorine ion in the mixture. The values of K_4 and K_5 are given in Table XXXVIII and it will be seen that there is still no constancy among them.

This lack of constancy and the general similarity between this transformation and an ordinary electrolytic dissociation led us to apply the Storch-Bancroft modification of the concentration law to our results. We first plotted the logarithmic form of the equation and obtained an approximate straight line which gave a value of $n/2 = 0.73$. The original equation would then become

$$(C_R \times C_{Cl'})^{0.73}/C_P = K_6.$$

The values of K_6 calculated for each mixture are given in Table XXXVIII. It will be seen that an approximate constancy is now attained. The constancy is particularly marked in those experiments where the concentration of the hydrochloric acid is relatively small and the inaccuracy of our method of calculation correspondingly less (Nos. 1, 2 and 7). This value of $n/2 = 0.73$, or $n = 1.46$ agrees excellently with the values 1.40–1.50 which Noyes and his co-workers have found to apply to the dissociation of all types of strong electrolytes.

Influenced by the somewhat arbitrary procedure of assigning exactly the same exponent to both anion and cation in the Storch-Bancroft equation when applied to mixtures, we tried varying the exponents of C_R and $C_{Cl'}$, keeping their sum equal to 1.46—since this total exponent would be expected when the equivalent concentrations of the two ions is the same; that is, when no foreign chlorine ions were present. The values calculated from this equation

$$C_R \times C_{Cl'}^{0.46}/C_P = K_7$$

are given in Table XXXVIII and show a very decided constancy. Its significance cannot be definitly settled until similar calculations have been made on ordinary dissociations.

The above calculations certainly indicate that the equilibria between roseo and purpureo chloride are comparable with the dissociation equilibria of strong electrolytes. It seems to differ from them only in the fact that the rate of reaction is measurably slow. It is because of this slowness of reaction that we are able to get the roseo salt out of solution and study it, without the chlorine ion getting back into the complex.

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As a result it has been shown that the splitting off of an additional chlorine ion from the purpureo molecules or ion is necessarily accompanied by a substitution of a water molecule in its place within complex.

By analogy, then, a similar process would be predicted for the dissociation of electrolytes in water, that is, hydration would necessarily accompany dissociation. This conclusion is in agreement with much recent work on aqueous electrolytes. A more rigorous test of all of these conclusions will only be possible when more certain information can be secured regarding the dissociation of the roseo and purpureo chlorides in the equilibrium mixtures.

The Free Energy Change.

This free energy change per mole for an ordinary reversible reaction is given by the simple expression RT *ln K*. That this also represents the free energy change in the present case where the equilibrium is not governed by the ordinary concentration law can be seen from the following consideration:

The free energy gain of the system when a mole of the purpureo compound changes from unit concentration at constant temperature to the equilibrium concentration C_P is equal to RT *ln* C_P. The energy required to bring one mole of chlorine ion and one mole of roseo salt from the equilibrium concentration C_R to unit concentration is equal to $2\int_1^{C_R} P_R dC_R$, or since P_R is a function of C_R to $2\int_1^{C_R} f(C_R)dC_R$. (We cannot assume the gas law to apply to these charged ions.) The free energy gained by the system when one mole of purpureo salt is converted into roseo and chlorine ion is then

$$W = -2\int_1^{C_R} f(C_R)dC_R + RT\, ln\, C_P. \qquad (1)$$

$$\text{But } C_R^{1.43}/C_P = K. \qquad (2)$$

$$\therefore \quad W = -2\int_1^{C_R} f(C_R)dC_R + RT\, ln\, C_R^{1.43} - RT\, ln\, K.$$

Differentiating

$$2f(C_R)dC_R = 1.43\, RTdC_R/C_R$$

or

$$2f(C_R) = 1.43\, RT/C_R.$$

Substituting in (1)

$$W = -1.43\, RT\int_1^{C_R} dC_R/C_R + RT\, ln\, C_P$$

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or

$$W = -RT \ln K.$$

K in the above calculation can be either K_0 or K_7—for the expressions containing these two constants become identical when a pure solution of the ammines is used. At present then, since K_7 gives the better constancy, we may substitute it in an approximate calculation of the free energy change. We should then have

$$W = -RT \ln K_7$$
$$= 275 \text{ cal.}$$

The affinity of the reaction would then be —275 cal. This can, of course, only be considered a preliminary calculation, pending a more accurate knowledge of the dissociation conditions in the equilibrium mixtures.

Measurements of Other Equilibria.

Several other pentammine cobalt salts were studied in the same way as the chloride. Attempts were made, for instance, with the nitrato-pentammine nitrate to discover whether or not an equilibrium existed between it and the corresponding roseo salt. We found that "nitron" was an excellent precipitant of the free nitrate ion, but it was difficult to filter and wash the precipitate rapidly. Our previous experiments have shown that the first filtration must be immediate and rapid. For the time being, therefore, the study of this equilibrium has been abandoned.

The purpureo bromide-roseo bromide equilibrium was, however, measured with more success. When a 0.01302 molar solution of purpureo bromide in 0.02 molar hydrobromic acid at 70° was analyzed by the precipitation of silver bromide, an equilibrium was found corresponding very nearly to pure roseo salt. Similar results were obtained starting with an equivalent solution of the roseo salt. The data is given in Tables XXXIX and XL, and in Curve II, Fig. V.

TABLE XXXIX.—EQUILIBRIUM MEASUREMENTS ON A 0.01302 MOLAR SOLUTION OF BROMOPENTAMMINE COBALT BROMIDE IN 0.02 MOLAR HYDROBROMIC ACID AT 70°.

No.	Weight of purpureo Salt. Gram.	Time of heating. Hours.	Weight of second precipitate of AgBr. Gram.	Percentage roseo.
73	0.5000	0.16	0.0221	85.25
74	0.5000	0.33	0.0093	96.12
75	0.5000	1.00	0.0093	96.20
76	0.5000	9.0	0.0062	97.46
77	0.5000	20.0	0.0046	98.11
78	0.5000	24.0	0.0047	98.10

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TABLE XL.—EQUILIBRIUM MEASUREMENTS ON A 0.01302 MOLAR SOLUTION OF PENTAMMINE COBALT BROMIDE (ROSEO) IN A 0.02 MOLAR SOLUTION OF HYDROBROMIC ACID AT 70°.

No.	Weight roseo Salt. Gram.	Time of heating. Hours.	Weight of second precipitate of AgBr. Gram.	Percentage roseo.
79	0.5237	0.10	0.0015	99.39
80	0.5237	1.05	0.0057	97.62
81	0.5237	9.0	0.0047	98.10
82	0.5237	14.0	0.0044	98.23
83	0.5237	30.0	0.0039	98.40

It will also be observed that the adjustment of equilibrium is much more rapid here than in the case of the chloride. This agrees with the velocity experiments described at the beginning of this paper. There is also a very slight decomposition indicated by the slight steady increase in the percentage of roseo salt during the last 21 hours.

We have also made some preliminary determinations upon the pentammine sulfato-sulfate equilibrium, but we are somewhat in doubt regarding the purity of the salts used. An equilibrium is, however, undoubtedly reached. The results obtained are given in Tables XLI and XLII and in Curve I, Fig. V.

TABLE XLI.—EQUILIBRIUM MEASUREMENTS IN A 0.0087 MOLAR SOLUTION OF SULFATOPENTAMMINE COBALT SULFATE IN 0.01 MOLAR SULFURIC ACID AT 70°.

No.	Weight of purpureo salt. Gram.	Time of heating Hours.	Weight of second precipitate of $BaSO_4$. Gram.	Percentage roseo.
84	0.5000	10	0.2281	43.8
85	0.5000	24	0.2294	43.5
86	0.5000	30	0.2274	44.0

TABLE XLII.—EQUILIBRIUM MEASUREMENTS ON A 0.00865 MOLAR SOLUTION OF SULFATOPENTAMMINE COBALT SULFATE (ROSEO) IN 0.01 MOLAR SULFURIC ACID AT 70°.

No.	Weight of roseo salt. Gram.	Time of heating. Hours.	Weight of second precipitate of $BaSO_4$. Gram.	Percentage roseo.
87	0.5266	3	0.2298	42.9
88	0.5266	24	0.2282	43.3
88	0.5266	30	0.2282	43.3

The Transformation in the Dry State.

Gibbs[1] in his original communication states that roseo chloride changes on standing into purpureo chloride. Jörgensen[2] has made use of a similar change in the case of the roseo nitrate to prepare purpureo nitrate.

[1] "Researches on the Ammonia Cobalt Bases." Smithsonian Contributions to Knowledge. Washington (1856), p. 9.

[2] *Z. anorg. Chem.*, 17, 160.

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This change of roseo into purpureo must be accompanied by an evolution of water vapor. We wished to find whether this water came off with a definit pressure at a given temperature; whether, in other words, the roseo salts possessed a definit aqueous vapor pressure. If this proved to be the case, we wished also to find out whether the process was reversible, *i. e.*, whether the roseo could be made from the purpureo salt in the dry state.

To measure first the aqueous vapor pressure we exposed weighed samples of roseo chloride, freshly prepared, over solutions of sulfuric acid of various concentrations. The weighed portions of the salt were placed upon small watch glasses supported by glass triangles over the sulfuric acid solutions in small stender dishes. Ground-glass covers were fitted tightly on the stender dishes and they were placed in desiccator jars, which were completely submerged in a thermostat, kept at 25°. If the change from purpureo to roseo salt, and *vice versa*, is analogous to the formation and dehydration of a salt hydrate, then the roseo salt at a constant temperature should exhibit a constant vapor pressure, and should steadily lose water to any solution of sulfuric acid having an aqueous vapor pressure lower than this. The purpureo salt, on the other hand, should steadily gain in weight when exposed to any solution of sulfuric acid having a higher aqueous vapor pressure than that of the roseo salt.

Two series of such experiments were carried out, the results of which are given in Tables XLIII and XLIV. The weighings in the second series (Table XLIV) are the more accurate, having been made on an assay balance and the differences in the concentration of the sulfuric acid are much less.

TABLE XLIII.—CHANGE OF ROSEO TO PURPUREO CHLORIDE IN THE DRY STATE AT 25°. TOOK 0.2000 GRAM.

No.	H_2SO_4. Per cent.	Loss in weight. (Milligrams.) 2 days.	4 days.	37 days.	68 days.	Per cent. conversion by loss.	Weight 1st AgCl. Gram.	Weight 2nd AgCl. Gram.	Total weight AgCl. Gram.	Per cent. conversion by analysis.	Remarks.
1	92.4	0.4	0.6	10.4	11.7	92	0.2272	0.086	0.3140	91.0	There was a marked color change between 4 and 5.
2	77.4	0.5	0.5	..	12.4	98	0.2305	0.0844	0.3149	78.8	
3	68.1	0.5	0.5	8.5	11.5	87	..	0.0828	..	77.7	
4	58.3	0.3	0.2	3.2	11.5	87	0.2314	0.0825	0.3139	77.9	
5	46.9	0.4	0.3	2.9	..	..	..	..	..	..	
6	32.3	0.2	0.1	0.5	3.5	28	0.2745	0.0405	0.3150 (calc. = 0.3160)	37.2	

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TABLE XLIV.—CHANGE OF ROSEO TO PURPUREO CHLORIDE IN DRY STATE AT 25°. TOOK 0.2000 GRAM.

No.	H_2SO_4. Per cent.	Loss in weight. (Milligrams.) 4 days.	7 days.	12 days.	24 days.	27 days.	Per cent. conversion (27 days).	Remarks.
7	65	0.42	0.84	1.84	6.04	8.14	64	There was a marked color change between 9 and 10.
8	61	0.48	0.94	2.64	4.54	6.28	50	
9	57	0.02	0.32	0.90	1.56	4.28	34	
10	53	0.02	0.02	0.20	1.40	1.90	15	
11	49	0.02	0.02	0.38	0.78	1.38	11	
12	44	0.10	0.12	0.32	0.80	1.04	8	

There is evidently a steady loss taking place over all the different strengths of sulfuric acid. There is, however, a very marked change in the amount lost between Nos. 4 and 5. There was also a very decided difference in color between these two samples; Nos. 5 and 6 retained the characteristic red color of the roseo salt, while Nos. 4, 3, 2 and 1 had all acquired the purple color of the purpureo salt. Similarly (Table XLIV) there was a marked color change between 9 and 10. This indicates that the critical point lies at about 55 per cent. sulfuric acid, and this acid solution has an aqueous vapor pressure of 5.1 mm. Hg. There is apparently then a definit pressure of water vapor from the roseo salt at this temperature, but a slow loss of water seems to take place at a much higher aqueous vapor pressure. It will be observed that the analytical results for the extent of the conversion agree with those calculated from the loss in weight as closely as could be expected. A similar experiment was tried to study the change from purpureo to roseo over the same strength of acid. The result is given in Table XLV.

TABLE XLV.—CHANGE OF PURPUREO ROSEO CHLORIDE IN DRY STATE AT 25°. TOOK 0.2000 GRAM.

No.	H_2SO_4. Per cent.	Loss in weight, 49 days. Milligram.	Remarks.
13	65	0.38	
14	61	0.38	
15	57	0.36	No change in color evident.
16	53	0.36	
17	49	0.35	
18	44	0.04	

It is seen that instead of a gain in weight over the more dilute acid there is a loss equal to that over the stronger. This indicates either that at 25° the reverse change does not take place in the time interval covered by the experiment or the equilibrium lies very near pure purpureo. The slight loss in weight was probably due to a trace of adsorbed moisture in the original salt. The reaction then, between roseo and purpureo chloride in the dry state is not a reversible one. It is possible, however, that the change to roseo salt, for instance, occurs in two stages: an intramolecular rearrangement and a subsequent com-

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bination with water. If this is the case, a pure sample of purpureo salt might change into roseo, even in the absence of water. We had fortunately an old sample of purpureo chloride of known purity, having been prepared in this laboratory by the sodium pyrophosphate method of Jörgensen in 1908. Two analyses of this salt gave respectively 98.5 and 98.7 per cent. purpureo modification. The very small percentages of roseo, 1.5 and 1.3, may well have been caused by the slight unavoidable transformation which takes place while getting the salt into solution, even though the temperature was kept at 0° during the process. Thanks to the courtesy of Professor G. P. Baxter, we also examined a sample of purpureo chloride prepared by Gibbs (probably about 1875). It was unfortunately very evidently impure, containing particles of a black substance. Two analyses showed that it contained 84.9 and 85.1 per cent. respectively of purpureo chloride. We can, however, draw no inferences from this sample. We must conclude then that in the absence of water no change to roseo salt results, even after a very long time, and that therefore the change to roseo salt and the absorption of water are necessarily concomitant processes.

Similarly, an experiment was made in order to find out whether roseo chloride would change to purpureo when no water was allowed to escape. For this purpose a freshly prepared sample of roseo chloride was first analyzed for purpureo, then sealed in a small glass tube, allowed to stand for a month, and then again analyzed. The first analysis gave 98.83 per cent., the second 98.84 per cent. roseo. This shows again that the transformation is necessarily connected with the liberation of the water.

Vapor pressure experiments with the roseo bromide and roseo nitrate indicated an aqueous vapor pressure about 4 mm. Hg each.

Summary.

In this paper we have studied the mutual transformation of the acidopentammine cobalt salts (purpureo) into the corresponding aquopentammine salts (roseo).

The velocities of transformation of various of these ammines in dilute aqueous solution were measured and it was found that they agreed with the requirements for a monomolecular reaction. They were but little affected by the acidity of the solution, thus distinguishing these transformations from the color changes of chromium salts. The velocity of transformation of the acido radical was also found to be independent of the radicals outside of the complex.

The rate of decomposition of these ammines was determined at various temperatures and in different solutions, and the amount of reduction which accompanied this decomposition was also determined both by a specially designed analytical method and by a study of the gaseous products of the decomposition.

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On the basis of this study of reaction and decomposition velocities, we selected 70° as the optimum temperature for equilibrium measurements. Working at this temperature we showed that our method of analysis was efficient, and that a true equilibrium was established in the solution. Selecting the chloride for a more extended study we varied the concentrations both of the reacting substances and of the other chlorides present and showed that the equilibrium is affected both by the total concentration of the salt and by the concentration of the chlorine ion; it is, however, independent of the acidity of the solution.

We calculated the concentrations of the various molecular species present in the equilibrium mixtures and applied the simple concentration law to the various possible equilibria which might exist between them. No satisfactory equilibrium constant was obtained. When, however, the equilibrium was viewed as an electrolytic dissociation of purpureo compounds into roseo compounds and chlorine ions, and their concentrations were substituted in the Storch-Bancroft modification of the concentration law, an approximate constant was obtained; a further modification of this law gave an excellent constant. We pointed out that if this view is correct we have the interesting case of a *slow* electrolytic dissociation. Furthermore, we know that the chlorine ion given off by the purpureo radical is replaced by a water molecule; by analogy the same thing would be expected in the dissociation of an ordinary electrolyte.

Finally, it was shown that in the dry state the roseo salts have a critical aqueous vapor pressure above which only a very slow loss of water occurs. The change does not appear to be reversible. It was further shown that the change is necessarily connected with the absorption or evolution of water.

We are carrying out measurements, similar to those described in this paper, on the ammines of chromium, iridium and rhodium and on the complex salts of cobalt and other metals with ethylenediammine.

NEW YORK CITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

A RE-INVESTIGATION OF THE VELOCITY OF SUGAR HYDROLYSIS.

FIRST COMMUNICATION.

BY M. A. ROSANOFF, R. H. CLARK, AND R. L. SIBLEY.

Received October 14, 1911.

1. Introductory.

The mechanism of sugar hydrolysis is as yet scarcely understood. Even as to the number of molecules that take part in the hydrolysis physico-chemical literature contains but incomplete information. Most investigators have, namely, found the reaction to be monomolecular with respect to sugar. There is some evidence also that the process in-

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volves the catalytic activity of one hydrogen ion. Finally, it is believed that the reaction is monomolecular with respect to water; but on this last point there are no experimental data.

In 1904 Armstrong and Caldwell[1] published a study of the hydrolysis of cane sugar by very dilute acids, from which it appears that even with respect to the sugar the reaction is not strictly monomolecular throughout its course, that in the earlier stages the reaction does not obey the mass law at all; the velocity coefficient showing a regular *increase*. Armstrong and Caldwell's measurements were numerous and skilfully carried out.

Four years later Julius Meyer[2] carried out similar measurements and likewise found the velocity coefficient changing during the early stage of the reaction. Meyer's coefficients, however, showed, not an increase, but a gradual *decrease*. Meyer believed that his results could be fully explained by assuming that the hydrolysis is complicated by a pair of side reactions taking place simultaneously with it: namely, the mutarotation of glucose and of fructose.

Meyer's measurements have been criticized by Hudson,[3] who justly points out that mutarotation can only lead to an *increasing* velocity coefficient, although, on the other hand, increase of the coefficient might also be caused by variation of the specific rotation of fructose with its concentration. He believes that Meyer's decreasing coefficients can only be explained by experimental errors. He agrees, however, that "the hydrolysis of cane sugar is not the simple reaction that it has heretofore been supposed to be, but is accompanied by two other important reactions."[4]

Hudson[5] accepts Armstrong and Caldwell's results, but thinks "the matter still in doubt as to whether Armstrong and Caldwell's deviation is due to mutarotation, change of rotation of fructose, or a true exception to the law of mass action, which latter view is the one that Armstrong and Caldwell hold."

That sugar hydrolysis is either a complex process, or else forms an exception to the law of mass action, might also be concluded from a phenomenon described by Ostwald a quarter of a century ago.[6] If the hydrolysis is monomolecular with respect to sugar, and the amount of water present is relatively large, the rate of the reaction should follow the monomolecular equation of mass action. According to this equation, the velocity coefficient must be independent of the initial concentration

[1] *Proc. Roy. Soc. London*, 74, 195 (1904).
[2] *Z. physik. Chem.*, 62, 59 (1908); see also *Ibid.*, 72, 117 (1910).
[3] THIS JOURNAL, 30, 1165 (1908); 32, 885 (1910).
[4] *Ibid.*, 32, 886 (1910).
[5] *Ibid.*, 889.
[6] *J. prakt. Chem.*, 31, 316 (1885).

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of the sugar. Ostwald, however, states that the velocity coefficient increases rapidly with the initial sugar concentration. For example, using hydrochloric acid of one and the same concentration (0.5 normal) as a catalyzer, he obtained:

Initial concentration of sugar. Per cent.	Velocity coefficient k.
4	19.14
10	20.63
20	22.87
40	29.16

In connection with these figures Ostwald observes: "The velocity constants change with the quantity of sugar almost in the ratio of three to two. It is, therefore, doubtless that the process of inversion is subject to the influence of side reactions, which manifest themselves the more clearly, the more concentrated the solutions."

Figures similar to Ostwald's have been published by Spohr.[1] A theory of the variation has been introduced by Arrhenius.[2]

2. Does the Velocity of Sugar Inversion Depend upon the Initial Concentration of the Sugar?

The first part or our re-investigation of the subject deals with the role played by the sugar and is reported in the present communication.[3]

The comparative measurements of Ostwald, Spohr, and others were carried out on solutions prepared in a manner equivalent to adding equal amounts of acid to equal volumes of a standard sugar solution and diluting with water, respectively, to twice, four times, etc., the original volume. The solutions of unequal sugar concentrations were, therefore, equally concentrated with respect to acid. But they contained *unequal quantities of water* per unit volume.

The effect of unequal quantities of water upon the catalytic power of an acid is as yet unknown. And so it seemed desirable to carry out new measurements, keeping the concentrations of both acid and water constant. Such is very nearly the case during the hydrolysis of any one given solution, and then the velocity coefficient remains constant. This constancy has been explained by assuming that the invert sugar, which gradually replaces the cane sugar, has a specific catalytic influence, similar to that of cane sugar itself, upon the rate of hydrolysis.

In order to ascertain more definitly whether the cause lies in such a specific influence of invert sugar, or in the constancy of the concentration of both acid and water, we prepared three pairs of solutions, acid

[1] *J. prakt. Chem.*, 33, 266 (1886).

[2] *Z. physik. Chem.*, 28, 319 (1899). See also Ernst Cohen, *Ibid.*, 23, 442 (1897).

[3] Further parts, dealing with the role played by water, acid, and neutral salts, will follow in communications from these laboratories as soon as practicable.

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and water having exactly the same concentration in each pair, but the sugar in one solution of each pair being replaced, in part, by glucose, mannitol, or acetone. In order to make the volumes of two solutions of a pair exactly alike, preliminary experiments were carried out, to show how much glucose, or mannitol, or acetone, as the case might be, must be added in place of part of the cane sugar to make the volume equal to that of the comparison solution containing none of the foreign substance. These data enabled us to weigh out precisely the quantities of the ingredients needed for every final experiment, warm them separately to the required temperature, and mix them rapidly at the beginning of the experiment. The rotations during hydrolysis were measured, for the most part, with an excellent half-shade quartz wedge compensation saccharimeter kindly placed at our disposal by Dr. William D. Horne, of the National Refining Company, Yonkers, N. Y. We wish to express here again our gratitude to Dr. Horne for his courtesy and generosity.

The temperature of the reacting mixtures was kept constant at 30° ± 0.02°. To avoid disturbances, the rotations were observed at the same temperature, 30°, the instrument used being inclosed in a wooden box within which this temperature was maintained sufficiently constant. Under these circumstances, our results can have no claim to high precision, but they are precise enough for the purposes of the problem. Kahlbaum's best formic acid, which we found to be 99.2 per cent. strong, was used in all except our two acetone experiments (an approximately 85 per cent. commercial acid was used in the acetone series). No further purification was required, for obvious reasons.

The results which we were aiming to obtain would plainly be the more decisive the greater the difference between the initial sugar concentrations of each pair of solutions. In our experiments these differences were limited by the solubilities involved.

In the tables below, t denotes the time in hours, α is the rotation ob-

TABLE I.—THE SOLUTION CONTAINED 50.500 GRAMS CANE SUGAR, 195.73 GRAMS WATER, AND 28.750 GRAMS FORMIC ACID (99.2 PER CENT.) IN 250 CC.

t.	α.	k.	t.	α.	k.
0	[78.00°]	..	37	6.45	0.0150
2	71.00	0.0159	42	2.30	149
3	68.10	152	48	— 1.95	149
4	65.10	151	52	— 4.05	147
5	62.30	150	61	— 9.00	149
7	56.70	150	72	—12.90	150
9.5	50.55	148	86	—15.80	147
12	44.60	149	95	—17.25	150
15	38.25	148	112	—19.30	154
18	32.40	148	∞	—21.15	..
21	27.35	148			
24	22.45	149		Average,	0.0150
28	17.10	148			

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served, and k is the velocity constant of the monomolecular mass law equation, calculated by the formula

$$k = \frac{1}{t} \log_{10} \frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty},$$

where α_0 and α_∞ denote, as usual, the initial and final rotations respectively. The initial rotations ($t = 0$), enclosed in brackets, were *calculated* as explained in Section 3.

TABLE II.—THE SOLUTION CONTAINED 14.250 GRAMS CANE SUGAR, 35.000 GRAMS GLUCOSE, 195.73 GRAMS WATER, AND 28.750 GRAMS FORMIC ACID IN 250 CC.

t.	α.	k.	t.	α.	k.
0	[66.40°]	..	24	50.75	0.0152
2	64.60	0.0151	27	49.65	151
3	63.70	152	31	48.35	150
4	62.90	150	37	46.70	148
5	62.10	149	43	45.20	149
6.5	60.90	150	51	43.65	149
8	59.80	150	55	43.05	150
10	58.50	147	64	41.70	155
12	57.10	150	75	40.70	150
18	53.55	152	89	40.05	155
21	52.15	151	∞	38.90	..
				Average,	0.0150

The velocity coefficients in the two comparison series given by Tables I and II are obviously identical. The initial sugar concentrations are in the ratio of 3.54 to 1.

TABLE III.—THE SOLUTION CONTAINED 37.613 GRAMS CANE SUGAR, 203.44 GRAMS WATER, AND 28.750 GRAMS FORMIC ACID IN 250 CC.

t.	α.	k.	t.	α.	k.
0	[57.90°]	..	24	16.95	0.0148
1	55.10	0.0169	27	13.50	149
2	53.15	146	31	10.10	146
3	50.80	147	35	6.75	148
4	48.50	149	40	3.40	147
5	46.50	147	46	— 0.40	149
6	44.40	147	52	— 2.95	148
8	40.50	147	60	— 5.90	147
9	38.70	146	66	— 7.45	146
11	35.20	146	74	— 9.40	146
13	31.80	147	85	—11.25	146
15	28.90	146	95	—12.60	149
18	23.80	145	112	—13.80	147
21	20.70	146	∞	—15.45	..
				Average,	0.0147

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TABLE IV.—THE SOLUTION CONTAINED 14.250 GRAMS CANE SUGAR, 22.000 GRAMS MANNITOL, 203.44 GRAMS WATER, AND 28.750 GRAMS FORMIC ACID IN 250 CC.

t.	*α.*	*k.*	*t.*	*α.*	*k.*
0	[22.10°]	..	30	4.50	0.0147
1	21.10	0.0160	34	3.25	147
2	20.30	146	39	1.90	146
3.5	19.00	148	45	0.35	149
5	17.85	145	51	—0.55	149
8	15.60	146	59	—1.80	146
10	14.15	148	65	—2.50	148
12	12.90	147	73	—3.20	148
15	11.10	147	84	—3.90	148
17	10.05	146	94	—4.30	147
20	8.65	145	111	—4.85	145
23	7.25	146	133	—5.10	147
26	6.00	146	∞	—5.50	..
				Average,	0.0146

The velocity coefficients in the two comparison series given by Tables III and IV are again equal. The initial sugar concentrations are in the ratio of 2.64 to 1.

A third pair of solutions, with acetone used to equalize the volumes, and again with the acid and water concentrations equal, gave a similar result: the two velocity coefficients were practically identical. In this case it seemed desirable to have some acetone in both solutions, to avoid too abrupt a difference in the nature of the reacting medium. An aqueous commercial acid was employed. Unfortunately, the determination of its exact strength was prevented by accident, and therefore the measurements will not be reported in detail.

The results given in Tables I to IV (together with the results of the acetone series just mentioned) show that the constancy of the velocity coefficient of sugar hydrolysis is not due to any specific effect of the invert sugar which gradually replaces the cane sugar in an ordinary single experiment. Glucose, mannitol, and acetone, and presumably any other inert substance, may be introduced in place of more or less of the cane sugar, and the velocity coefficient will be the same, as long as the concentrations of both water and acid remain unchanged. The velocity coefficient is independent of the initial concentration of the sugar itself.

3. Do Armstrong and Caldwell's Results Indicate Either Side Reactions or Deviation from the Law of Mass Action?

As before stated, Armstrong and Caldwell found a regular increase of the velocity coefficient *in the early stages* of sugar hydrolysis. The following circumstance, however, led us to suspect that their varying values of *k* might be only apparent; due, not to complicating side-reactions,

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or deviations from the mass law, but to slight errors in the assumed values of α_0. If, namely,

$$k = \frac{1}{t} \ln \frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty},$$

then, for a given set of values of t, α, and α_∞ (since slight changes of α_0 leave the difference $\alpha_0 - \alpha_\infty$ practically constant),

$$\frac{dk}{d\alpha_0} = \frac{1}{t(\alpha_0 - \alpha_\infty)} = \frac{1}{t} \times \text{constant}.$$

In words: the effect of an error in the initial reading α_0 upon the value of the velocity constant k is inversely proportional to the time elapsed since the beginning of the reaction. This means that even a slight error in the value of α_0 assumed in computing k is liable to lead to grossly erroneous values of k for the earliest stages of the reaction (especially in dilute solutions, where $\alpha_0 - \alpha_\infty$ is small). The error rapidly decreases and becomes inappreciable for the more advanced stages of the reaction.

A far more reliable value of α_0 than can be obtained by direct observation may be calculated as follows: The ordinary monomolecular equation

$$k = \frac{1}{t} \log_{10} \frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty}$$

is written in the form

$$\log_{10}(\alpha - \alpha_\infty) = A + Bt;$$

the best values of A and B are obtained by applying the method of least squares to all the observations of a given series, and α_0 is readily found from $A = \log_{10}(\alpha_0 - \alpha_\infty)$. The value of α_0 is then as reliable as that of α_∞, which can be observed at leisure with all possible care.

Another way, based on the same principle, consists in plotting, on as large a scale as possible, the available values of $\log_{10}(\alpha - \alpha_\infty)$, against the corresponding values of t, and extrapolating to $t = 0$ to find $\log_{10}(\alpha_0 - \alpha_\infty)$, and hence α_0. *Armstrong and Caldwell's results, when plotted in this manner on a large scale, yielded perfectly straight lines for all series, without the slightest indication of curvature anywhere* (see Table IX), *demonstrating sugar hydrolysis to be a simple reaction, monomolecular with respect to sugar, and free from disturbing* (*i. e., relatively slow*) *mutarotation reactions or other side-reactions throughout its course* (see Section 4 below).

The figures given in the following tables were obtained from values of α_0 (enclosed in brackets) yielded by the method of least squares. That Armstrong and Caldwell's observed values of α_0 are erroneous, and that our calculated values are much more reliable, is clearly indicated by the data reproduced in Tables V and VI. The solutions corresponding to these tables had identically the same final rotation, $-5.37°$, and hence must have been identical in composition. Yet the observed initial ro-

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tations were respectively 22.22° and 22.12°. On the other hand, our calculated values, 22.28° and 22.26°, are practically equal.[1]

TABLE V.—ARMSTRONG AND CALDWELL'S RESULTS (*Loc. cit.*, p. 197) RECALCULATED.

t.	α.	k(A. & C.).[2]	k(recalc.).	t.	α.	k(A. & C.).[2]	k(recalc.).
0	[22.28°]	....	...	240	16.17	0.000448	0.000456
15	21.83	0.000412	(0.000472)[3]	255	15.78	453	458
30	21.40	437	(467)	270	15.43	454	462
45	21.00	437	456	285	15.05	459	456
60	20.63	430	445	345	13.87	455	456
75	20.18	445	457	360	13.57	454	458
90	19.77	449	459	375	13.25	455	458
105	19.45	438	446	390	12.95	456	459
120	19.00	449	457	405	12.65	457	456
135	18.63	448	455	420	12.42	454	457
150	18.27	447	453	435	12.13	454	457
165	17.92	446	452	450	11.85	453	457
180	17.52	451	456	465	11.58	455	457
195	17.18	449	454	480	11.32	455	456
210	16.83	450	455	495	11.07	454	457
225	16.47	451	452	510	10.80	455	455
				∞	—5.37	..	....
						Average,	0.000456

TABLE VI.—ARMSTRONG AND CALDWELL'S RESULTS (*Loc. cit.*, p. 197) RECALCULATED.

t.	α.	k(A. & C.).[4]	k(recalc.).	t.	α.	k(A. & C.).[2]	k(recalc.).
0	[22.26°]	....	....	270	15.60	0.000435	0.000445
15	21.73	0.000414	(0.000564)	285	15.27	437	446
30	21.35	411	(486)	300	14.93	439	446
45	20.97	412	(462)	315	14.63	438	447
60	20.58	417	455	330	14.30	441	444
75	20.22	415	455	345	13.95	444	449
90	19.82	422	447	360	13.68	442	448
105	19.45	423	444	375	13.35	443	448
120	19.03	431	450	390	13.10	445	449
135	18.72	425	441	405	12.83	442	447
150	18.37	425	440	420	12.53	444	449
165	18.00	427	441	435	12.23	445	450
180	17.60	433	446	450	11.97	445	450
195	17.23	436	448	465	11.73	443	448
210	16.90	435	446	480	11.48	443	448
225	16.60	433	443	495	11.23	443	447
240	16.27	433	442	510	11.03	440	444
255	15.93	434	444	∞	—5.37	...	...
						Average,	0.000447

[1] The decrease of the recalculated coefficients in the very beginning of the series in Tables V–VIII deserves no consideration, as there the coefficients are enormously affected by errors of α_0, α, and t. Under t in these tables time is expressed in minutes.

[2] Based on $\alpha_0 = 22.22°$.

[3] The average coefficient, 0.000456, would have resulted instead of 0.000472 if the observed rotation had been not 21.83°, but 21.85°.

[4] Based on $\alpha_0 = 22.12°$.

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TABLE VII.—ARMSTRONG AND CALDWELL'S RESULTS (*Loc. cit.*, p. 198) RECALCULATED.

t.	α.	k(A. & C.).[1]	k(recalc.).	t.	α.	k(A. & C.).[1]	k(recalc.).
0	[46.38°]	....	....	290	29.87	0.000498	0.000507
10	45.47	0.000428	(0.000692)	300	29.38	495	504
20	44.83	461	(593)	310	28.83	502	510
30	44.20	471	(559)	320	28.42	500	508
40	43.62	468	(534)	330	27.93	501	509
50	42.97	478	(531)	340	27.43	503	511
60	42.37	479	(523)	350	26.97	503	511
70	41.80	477	515	360	26.55	503	510
80	41.17	482	515	370	26.12	503	510
90	40.57	485	514	380	25.65	504	411
100	40.07	488	505	390	25.25	504	510
110	39.45	483	507	400	24.87	502	509
120	38.85	486	508	410	24.42	503	509
130	38.28	487	507	420	24.02	503	509
140	37.67	491	509	430	23.62	503	509
150	37.13	490	508	440	23.17	504	510
160	36.55	492	509	450	22.80	503	509
170	36.03	491	507	460	22.38	504	510
180	35.43	495	510	470	21.93	506	511
190	34.93	494	508	480	21.53	507	512
200	34.45	492	505	490	21.13	507	512
210	33.87	495	508	500	20.77	507	512
220	33.38	494	506	510	20.40	507	512
230	32.87	494	506	520	20.00	508	513
240	32.38	494	505	530	19.68	506	511
260	31.28	499	509	540	19.27	508	513
270	30.80	499	508	∞	—11.12	...	...
280	30.38	496	506				
						Average,	0.000509

TABLE VIII.—ARMSTRONG AND CALDWELL'S RESULTS (*Loc. cit.*, p. 198) RECALCULATED.

t.	α.	k(A. & C.).[2]	k(recalc.).	t.	α.	k(A. & C.).[2]	k(recalc.).
0	[44.89°]	....	....	230	31.13	0.000527	0.000537
10	44.02	0.000481	(0.000681)	240	30.65	526	534
20	43.37	489	(600)	250	30.13	527	535
30	42.75	493	(566)	260	29.62	528	535
40	42.20	487	539	270	29.08	530	537
50	41.58	492	531	280	28.60	530	536
60	40.93	500	531	290	28.15	529	535
70	40.30	505	533	300	27.63	530	537
90	39.10	507	530	310	27.22	528	535
100	38.47	512	532	320	26.72	530	536
110	37.87	513	531	330	26.28	529	535
120	37.28	515	531	340	25.83	529	535
130	36.70	516	531	350	25.32	532	537
140	36.13	516	531	360	24.88	532	536
150	35.53	519	533	370	24.47	531	536

[1] Based on $\alpha_0 = 46.03°$.

[2] Based on $\alpha_0 = 44.63°$.

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TABLE VIII (*continued*).

t.	α.	k(A. & C.).	k(recalc.).	t.	α.	k(A. & C.).	k(recalc.).
160	34.95	0.000521	0.000534	380	24.02	0.000532	0.000537
170	34.33	525	536	390	23.60	531	536
180	33.78	526	537	400	23.15	532	537
190	33.25	525	536	410	22.73	532	537
200	32.73	525	535	420	22.35	531	536
210	32.25	523	532	∞	—10.79	...	...
220	31.65	527	536				
						Average,	0.000535

To show how closely $\log_{10}(\alpha - \alpha_\infty)$ is represented by a linear function of t, we reproduce in Table IX the figures for one of Armstrong and Caldwell's series (the same as that of Table V). Under $\log_{10}(\alpha - \alpha_\infty)$ *obs.* are values based on the observations; under $\log_{10}(\alpha - \alpha_\infty)$ *calc.* are values calculated from the equation

$$\log_{10}(\alpha - \alpha_\infty) = 1.44165 - 0.0004562t.$$

TABLE IX.

t.	$\log_{10}(\alpha-\alpha_0)$ *obs.*	$\log_{10}(\alpha-\alpha_0)$ *calc.*	t.	$\log_{10}(\alpha-\alpha_0)$ *obs.*	$\log_{10}(\alpha-\alpha_0)$ *calc.*
15	1.4346	1.4348	255	1.3253	1.3253
30	1.4276	1.4280	270	1.3181	1.3185
45	1.4211	1.4211	285	1.3101	1.3116
60	1.4150	1.4143	345	1.2842	1.2843
75	1.4074	1.4074	360	1.2774	1.2774
90	1.4004	1.4006	375	1.2700	1.2706
105	1.3948	1.3937	390	1.2629	1.2637
120	1.3869	1.3869	405	1.2558	1.2569
135	1.3802	1.3801	420	1.2502	1.2500
150	1.3736	1.3732	435	1.2430	1.2432
165	1.3672	1.3664	450	1.2360	1.2364
180	1.3596	1.3595	465	1.2292	1.2295
195	1.3531	1.3527	480	1.2225	1.2227
210	1.3464	1.3458	495	1.2159	1.2158
225	1.3393	1.3390	510	1.2087	1.2090
240	1.3332	1.3322	525	1.2028	1.2021

4. Do Julius Meyer's Results Indicate Either Side Reactions or Deviation from the Law of Mass Action?

Meyer's velocity coefficients show a great decrease. If the variation were here again due to an erroneous α_0, it seemed reasonable to expect that the error was large enough to appear if the actual readings α were directly plotted against the corresponding times t. As a matter of fact, the accompanying figure, representing the data of Meyer's "*Tabelle 18*,"[1] shows that the curve of α's cannot possibly originate in the point representing the α_0 assumed by Meyer.

Table X reproduces the same series of Meyer's and shows that with a

[1] *Loc. cit.*, 62, 79.

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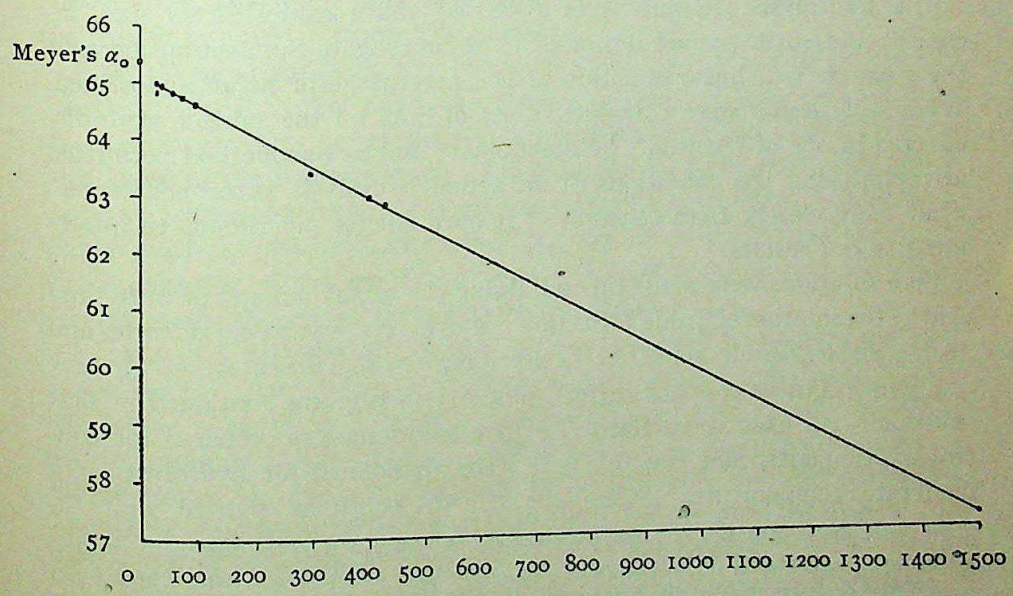
correct α_0 the velocity coefficient (k recalculated) is constant within the errors of experiment.[1]

TABLE X.—ONE OF JULIUS MEYER'S SERIES (*Loc. cit.*, 62, 79) RECALCULATED.

t (min.).	α.	k (Meyer).[2]	k(recalc.).
0	[65.09°]	....	.....
7	65.18(?)	0.000302	.....
10	65.14(?)	258	.....
24	64.96	195	0.0000275
38	64.88	151	280
55	64.80	119	269
72	64.71	106	269
98	64.58	95	266
296	63.38	79	297
400	62.89	73	283
430	62.81	70	270
1500	57.20	67	281
∞	—20.28	...	...
		Average,	0.0000277

Armstrong and Caldwell's, Meyer's, and our own measurements thus demonstrate that sugar hydrolysis proceeds in accordance with the law of mass action, as a reaction strictly monomolecular with respect to sugar.



Side-reactions comparable in speed with the hydrolysis proper would manifest themselves in deviations from the monomolecular equation, and hence if mutarotation, for instance, accompanies the hydrolysis at

[1] See also Hudson, THIS JOURNAL, 30, 1165 (1908).

[2] Based on α_0 = 65.36°.

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all, it must reach completion with relatively great rapidity and may be left out of account.[1]

This may suggest the conclusion that the *mechanism* of sugar hydrolysis is correctly described by the ordinary stoichiometric equation, single uncombined sugar molecules being hydrolyzed by water rendered active by the hydrogen ions of the catalyzer. But such a conclusion is not necessarily right. Indeed, the reaction would still follow the monomolecular equation if each single molecule undergoing hydrolysis were not sugar itself, but a compound of one (not more than one) sugar molecule with molecules of one or more other substances.

5. Does the Polariscope Show the True Composition of the Solution during Hydrolysis?

Hudson[2] points out that polarimetric analysis, which assumes that the partial rotations of sucrose, glucose, and fructose are proportional to their concentrations, involves a considerable error. The specific rotations of the three sugars vary appreciably with the concentrations, and that of fructose varies rapidly: "If the progress of the inversion is calculated from the polariscopic readings under the assumption that the specific rotation of fructose remains constant during the reaction, the velocity coefficient must be expected to increase."

The hydrolysis measurements discussed above exhibited no such increase; and so it seemed desirable to re-investigate the assumption that the rotation is a linear function of the percentage of sugar hydrolyzed. When our results were complete, a set of data on the subject were discovered in one of Ostwald's publications.[3] But as our method permitted of reproducing the conditions of an actual hydrolysis experiment somewhat more closely than Ostwald's,[4] it may not be superfluous to briefly mention our results.

Five solutions were made up containing the same amounts of water and acid as the solution of Table I (Section 2 above), *viz.*, 195.73 grams water and 28.750 grams formic acid, but respectively 7.500, 15.000, 22.500, 30.000, and 37.500 grams of sugar instead of the 50.500 grams contained in that solution. An exactly similar set of five solutions was prepared for control experiments, and the two sets were abandoned for hydrolysis at a moderate temperature. When the control solutions showed that in-

[1] That in the absence of acids, when sugar is hydrolyzed by the enzyme invertase, mutarotation reactions do accompany the hydrolysis and proceed with a speed not very different from that of the hydrolysis itself, has been shown by O'Sullivan and Thompson, *J. Chem. Soc.*, 57, 927 (1890), and by Hudson, THIS JOURNAL, 30, 1160 (1908).

[2] THIS JOURNAL, 32, 888 (1910).

[3] *J. prakt. Chem.*, 29, 390 (1884).

[4] Ostwald measured the rotation of solutions of known cane and invert sugar content after eliminating the catalyzing acid.

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version was complete, the following amounts of cane sugar were added to the five principal solutions (taken in the same order as above): *viz.*, 43.000, 35.500, 28.000, 20.500, and 13.000 grams. The temperature having been reduced to 30.00°, the five solutions were at that moment exactly like the solution of Table I at several stages of hydrolysis, with the percentages hydrolyzed precisely known. It remained to ascertain the corresponding rotations. Hydrolysis had set in anew with the addition of sugar, and now a series of rotation readings were taken, at intervals of 1 hour, for periods of 15 to 20 hours. The desired "initial" readings were found by a simple extrapolation method. *These readings lay unmistakably on a straight line*, which was best represented by the equation

$$\alpha = \alpha_0 - 0.01(\alpha_0 - \alpha_\infty)p = 78.19 - 0.9938p,$$

where p is the percentage hydrolyzed. The equation gives: $\alpha_0 = 78.19°$ and $\alpha_\infty = -21.19°$, in sufficient agreement, respectively, with the $\alpha_0 = 78.00°$ required by the figures of Table I and the $\alpha_\infty = -21.15°$ found by direct observation.[1]

6. The Variation of the Specific Rotatory Power of Fructose.

Ostwald's determinations, together with the results just mentioned, point to the conclusion that in a sugar solution in process of hydrolysis the specific rotation of fructose is constant.

Now, during hydrolysis the water concentration remains practically constant. On the other hand, in aqueous solutions of fructose used in a study of its rotatory power the water concentrations are varied together with those of the fructose itself. For instance, a 35 per cent. solution of fructose contains about 30 per cent. less water than an equal volume of a highly dilute solution. And so the idea suggested itself that the cause of the variation of the specific rotatory power of fructose may lie in the varying water content of the solutions employed.

By way of a first test of this idea, it was proposed to prepare a strong (about 35 per cent.) solution of fructose, and dilute it gradually with a solution of some other substance containing the same amount of water per unit volume as the fructose solution itself. In order to simplify the manipulations involved, it was decided to try as a diluting medium a solution of cane sugar of the same density as the fructose solution. Two such solutions were expected to prove nearly enough equal in water concentration and also to mix without contraction or expansion of volume.

An approximately 100-gram lot (undried) of Kahlbaum's fructose was dissolved in water, and the solution, diluted to 250 cc. at 17.5°, was abandoned for a considerable time, till at least the more rapid stages of mutarotation were over. It was then decolorized with bone black in the

[1] In angular degrees the differences amount to only 0.06° and 0.01°, respectively.

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cold. Its specific gravity at 17.5°, referred to water of the same temperature, was 1.1502.

Next a solution of cane sugar of the same density was prepared by dissolving 98.496 grams, (calculated by Arrhenius' formula) of sugar in water and diluting to 250 cc. at 17.5°. A specific gravity determination at that temperature gave 1.1501.

The quantities of water in the two solutions differed by less than 1 per cent. When equal samples of the two were mixed together, neither contraction nor expansion took place: the specific gravity of the mixture at 17.5° was found to be 1.1501.

It was thus possible, by mixing the two solutions in several different proportions, and observing the rotations of the mixtures, to determin whether the partial rotations of the fructose solution were proportional to the quantities of that solution in the mixture, and hence whether the specific rotation of fructose remained constant.

If the partial rotation of the fructose solution is proportional to its percentage in the mixture, then the total rotation (α) must be a linear function of that percentage (p). As a matter of fact, Table XI shows that the observed rotations are almost perfectly reproduced by the equation

$$\alpha = 24.54 - 0.5830p,$$

and hence, that the specific rotation of fructose in our mixtures was independent of its concentration. But this matter will be subjected here to further study.

TABLE XI.

p.	α *obs.*	α *calc.*	Diff.
0.00	+24.54°	+24.54°	±0.00°
10.41	+18.53	+18.47	—0.06
20.12	+12.78	+12.81	+0.03
30.04	+ 7.03	+ 7.03	±0.00
40.23	+ 1.09	+ 1.09	±0.00
60.03	—10.55	—10.46	+0.09
69.76	—16.17	—16.12	+0.05
89.69	—27.72	—27.75	—0.03

WORCESTER, MASS., June, 1911.

STUDIES IN CONDUCTIVITY. I. THE CONDUCTIVITY OF AMMONIA IN (ANHYDROUS) FORMIC ACID. I. "FORMIC ACID HYDROLYSIS."

BY H. I. SCHLESINGER AND R. P. CALVERT.

Received October 24, 1911.

In recent years, a great deal of attention has been given to the study of non-aqueous solutions, especially from the point of view of the theory of ionization. While this work has covered a wide range of solvents, the

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solutions investigated are, with but few exceptions,[1] solutions of salts. It is therefore very desirable that a similar, systematic study of acids and bases in solvents other than water should be made. The importance of such an investigation has been emphasized by a recent paper by Walden,[2] in which he suggests that in solvents of acid character bases should be highly ionized, and *vice versa*, provided that the other properties of the solvents tend to make them ionizing agents. In view of the special interest thus attached to solutions of acids and bases in solvents of varying chemical character, a study of the conductivity of such solutions has been undertaken. Although the work is as yet in the initial stages, some of the results have proved of sufficient interest in themselves to warrant their publication.

Formic acid, on account of its decidedly acid character in aqueous solution and its high dielectric constant, is a particularly favorable solvent for this investigation. The results of Zanninovich–Tessarin[3] indicate that, in agreement with Walden's postulate, acidic substances are but little ionized when dissolved in formic acid. In fact, the results for hydrogen chloride show an association rather than a dissociation. On account of the rather high initial conductivity of the formic acid employed in the investigations referred to, it is impossible to decide from them whether the latter reaction does not take place to a slight extent; for this reason this work is to be repeated in this laboratory. In order to test the other phase of the postulate mentioned, the conductivity of ammonia in the same solvent was studied.

The acid was prepared from Kahlbaum's 95 per cent. formic acid by repeated distillation from phosphorus pentoxide, at about 35° and a pressure of about 35 mm. of mercury.[4] After about nine distillations, the specific conductivity of the acid at 25° averaged 6.82×10^{-5}, and its freezing point was 8.60°. The latter constant was determined with all of the necessary precautions and a thermometer, compared with a standardized platinum resistance thermometer, was employed.[5] The freezing point obtained is slightly higher than the highest found in the previous literature, namely 8.50°.[6] The specific conductivity does not compare quite so favorably with other values, the lowest actually at-

[1] See, for example, Kablukov, *Z. physik. Chem.*, 4, 429. Zelinskii and Krapivin, *Ibid.*, 21, 35. Walden, *Ibid.*, 54, 129 and 43, 400, where other references may be found. Franklin, *Am. Chem. J.*, 23, 277, and THIS JOURNAL, 27, 191. Röhler, *Z. Elektrochem.*, 16, 419. See also below.

[2] *Trans. Far. Soc.*, 6, 71 (1910).

[3] *Z. physik. Chem.*, 19, 251 (1896).

[4] The acid is partially decomposed by this treatment.

[5] We are indebted to the kindness of Prof. Menzies for this calibration.

[6] Walden, *Loc. cit.* But Novak (*Phil. Mag.*, [5] 44, 828) arrives at the value 8.52° by extrapolation, from the freezing points of the aqueous acid.

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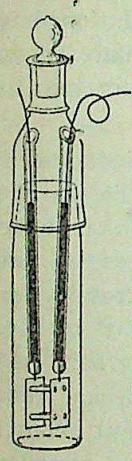
tained being about 3.7×10^{-5} at 18°.[1] Novak,[2] by an extrapolation based on the change of conductivity of the acid on the addition of water, derives the value 1.4×10^{-5} at 8.52° which corresponds to about $2-3 \times 10^{-5}$ at 25°, judging roughly from analogous calculations by Novak. That this acid of high freezing point is not the monohydrate as has been suggested by others, is shown by the results of titration of the acid against standard alkali. The mean of a large number of determinations gave 99.96 per cent. as the degree of purity. Owing to an apparent action of the acid upon the indicators, the results agreed to only 0.5 per cent., but this error can not affect the conclusion, since the monohydrate ($2HCOOH.H_2O$)[3] contains only 83.7 per cent. of acid.



One-third actual size.

Ammonia carefully dried over soda-lime and freshly cut sodium was passed into the acid. The strength of the resulting solution was determined by a modification of the Kjeldahl method. The conductivity was determined between platinized electrodes in the cell which is shown in the accompanying sketch. Resistances were measured by the usual Wheatstone-Kohlrausch method, with standardized resistances and a calibrated bridge. Constant temperature was maintained by placing the cell into a Freas thermostat adjusted at 25° ± 0.01 (hydrogen scale). The cell constant was determined by the use of both $N/50$ potassium chloride and $N/64$ sodium chloride.

In making the solutions of varying concentration, the method of employing two calibrated pipets, as it is described in the manuals, was used. The delivery pipet was calibrated first with water and then with formic acid but no appreciable difference in the volume delivered was found. The two pipets differed, for content and delivery, by less than 0.02 cc. in the total volume of 10 cc. This method of making up the solutions has the disadvantage that changes in density, as the solutions become more dilute, are not accounted for; but owing to the expense of the solvent and the relatively large amount of time required in purifying it, we considered it inadvizable to attempt to make up each dilution separately. In making the dilutions in this way there was also considerable chance of allowing the acid to absorb moisture: by having all materials in vessels with carefully ground stoppers and by the use of a pump and calcium chloride tubes in drawing the liquids into the pipets the danger from this source was decreased. In order to determin roughly

[1] Sapozhnikov, *J. Russ. Phys. Chem. Soc.*, 25, 629. The data are given in Siemens units in the original. The same is true of Novak's data.

[2] *Loc. cit.*

[3] Colles, *J. Chem. Soc.*, 89, 1251. The results of Kremann, *Monatsh.*, 28, 893, 900, make the existence of hydrates seem doubtful.

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how great the effect of absorbed moisture might be, pure formic acid was pipetted in and out of the cell exactly as was done in a conductivity determination. In a number of operations corresponding to five dilutions, the conductivity of the acid[1] changed from 11.96×10^{-5} to 12.09×10^{-5}, a change of 1 per cent., which is but little greater than the experimental error in the measurement of these small conductivities. For more accurate work, in which moisture must be more effectively excluded, a special cell has been constructed, which will be described in a later paper.

In Table I are given the experimental results for the conductivity of the ammonia solutions and a few calculations based upon them. The first column gives the concentration (c) in gram molecules per liter, the second the specific conductivities (κ) in reciprocal ohms,[2] the third the molecular conductivities (μ_v) calculated in the usual way. The figures in the remaining columns will be discussed below.

TABLE I.—CONDUCTIVITY OF NH_3 IN HCOOH AT 25°.

c.	κ.	μ_v.	μ'_∞. (Kohlrausch).	μ_∞. (Ostwald).	α.[4]	k.
			First Series.			
0.135	0.008717	64.57	...	...	0.899	1.09
0.0675	0.004572	67.73	79.92	71.86	0.943	1.05
0.03375	0.002351	69.66	78.28	71.75	0.970	1.05
0.01687	0.001196	70.90	77.24	72.02	0.987	1.24
0.00844	0.000591	70.02	73.53	[70.42]	..	..
0.00422	0.000274	64.93	65.09	[51.58]	...	..
0.00211	0.000122	57.82	...	...	...	..
0.00105	0.00005	47.39	...	...	...	..
.....	....	...	Mean[3]	71.87	...	1.11
			Second Series.			
0.55	0.02918	53.05	...	...	0.738	1.15
0.275	0.01647	59.89	86.18	71.90	0.834	1.15
0.1375	0.008850	64.37	83.64	(70.98)	0.896	1.05
0.06875	0.004675	68.00	82.95	71.86	0.946	1.15
0.03437	0.002399	69.80	80.87	71.84	0.972	1.14
0.01719	0.001216	70.73	79.22	71.77	0.984	1.07
0.00859	0.000603	70.16	75.86	[70.46]	...	..
0.00430	0.000283	65.86	69.03	[66.03]	...	..
0.00215	0.000123	57.30	...	...	...	..
0.00107	0.000052	48.72	...	...	...	..
...	...	...	Mean	71.840	...	1.12

In most aqueous solutions, the molecular conductivities rize continuously with increasing dilution or approach a constant maximum

[1] The best acid was not used in this test.

[2] Obtained from the observed conductivities by subtracting the specific conductivity of the acid used.

[3] Figures in parentheses or brackets were not included in the mean value.

[4] The value $\mu_\infty = 71.85$ was used in calculating α.

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value. It will be seen from the data in column 3 that for the solutions under discussion this is not the case: the values rize to a maximum and then decrease. Similar phenomena have been observed by others[1] in non-aqueous solutions and several explanations have been suggested. While this is therefore not an isolated case, the nature of the solutions makes a specific interpretation of the divergence from the normal behavior of aqueous solutions seem probable here. From the values of the specific conductivities it appears likely that the drop in molecular conductivity in the solutions for which the specific conductivity is comparatively low, is associated with the relatively high conductivity of the solvent. That this is not in itself sufficient to explain the character of the curve is shown by the values obtained for ammonium chloride solutions. These are appended, for the purpose of comparison in Table II (see p. 1931); although the specific conductivities of the greater dilutions given in this table are fully as small as those for the ammonia solutions, no decrease in the molecular conductivities is observed. In the ammonia solutions, however, there is reason to believe that the specific conductivity of the solvent cannot be considered to remain constant nor to have the value found by measuring the conductivity of the acid directly; for the ammonia solutions undoubtedly contain highly ionized ammonium formate, which, on account of the large concentration of formate ion which it yields, would tend to repress the ionization of the formic acid almost completely. It is nevertheless not permissible to assume that in the solutions the conductivity of the acid is entirely destroyed, because the acid used was probably not absolutely pure[2] and part of its conductivity must be ascribed to these impurities. A second factor may also prove to be a matter of importance: both the conductivity of the acid itself and that of the impurities may possibly be increased by a "salt effect." The latter would in the more concentrated solutions tend to counterbalance the "common ion" effect, so that the more concentrated solutions would give us the more reliable data. This must be true also because variations in the specific conductivity of the solvent would have a much smaller influence upon the value for concentrated solutions, since, for these the specific conductivity is sufficiently high to render the *percentage* error introduced by the conductivity of the solvent very small. The only data available for deciding upon a minimum value for the specific conductivity of the pure acid are those of Novak;[3] but since they refer to a much lower temperature than that of our experiments, it is not

[1] See, for example, Archibald, This Journal, 29, 674, where other instances are cited. Plotnikov, *J. Russ. Phys. Chem. Soc.*, 40, 1243. Walden, *Z. physik. Chem.*, 54, 133, suggests an explanation similar to the one given in this paper, for a different case.

[2] Pure acid should have a conductivity of $2-3 \times 10^{-5}$ (Novak, *Loc. cit.*); ours had a conductivity of 6.86×10^{-5}.

[3] *Loc. cit.*

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possible to make use of them for approximating the corrections suggested above. Consequently we are forced to leave out of consideration the values for the more dilute solutions, at least for the present, and to confine our attention to the more normal values of the more concentrated solutions. The following discussion is limited therefore to the concentrations for which rizing values for the molecular conductivities are obtained, *i. e.*, from 0.55 N to 0.01687 N.

For the interpretation of conductivity data several formulas are generally considered: the Ostwald dilution law; or, where this does not give satisfactory results, the equations of Kohlrausch, of Rudolphi, of van't Hoff or modifications of the last two. The use of any of these formulas in the usual way involves the knowledge of the value of the molecular conductivity at infinit dilution. For the reasons given this could not be determined experimentally. The formulas can however be used to calculate this value; if any one of them gives a constant for the conductivity at infinit dilution, the formula may be considered to apply to the case in question. In this way the first two of the equations mentioned were tried. The dilution law may be written as follows:

$$\frac{(\mu_1/\mu_\infty)^2 c_1}{1-\mu_1/\mu_\infty} = K_o; \qquad \frac{(\mu_2/\mu_\infty)^2 c_2}{(1-\mu_2/\mu_\infty)} = K_o;$$

in which c_1, c_2.....represent successive values for the concentration, μ_1, μ_2.....successive values for the molecular conductivity, μ_∞ the molecular conductivity at infinit dilution, and K_o is a constant. By eliminating K_o and solving for μ_∞, we get

$$\mu_\infty = \frac{\mu_1\mu_2^2.c_2/c_1 - \mu_1^2\mu_2}{\mu_2^2.c_2/c_1 - \mu_1^2}. \qquad \text{I.}$$

The equation of Kohlrausch may be transformed in like manner to read

$$\mu'_\infty = \frac{\mu_1 - \mu_2\sqrt[3]{c_1/c_2}}{1-\sqrt[3]{c_1/c_2}}. \qquad \text{II.}^1$$

By substituting different pairs of data for the concentration and the conductivity a series of values for μ_∞ can be calculated. The figures in the fourth column of the table are obtained in this way from equation II, those in the fifth column, from equation I.

It is clear that only the figures in the fifth column represent constant values. This is best shown in the second series where there are more data for comparison. In the two series there is but one value, of those under consideration, which differs from the mean by more than 0.3 per cent., an excellent agreement. From the average of the values of μ_∞ so obtained the degree of dissociation, $\alpha(=\mu_v/\mu_\infty)$, and K_o can be calculated. These are given in columns 6 and 7 of the table. Although

[1] The Kohlrausch equation is usually stated in terms of equivalent conductivities. In the present instance this value is identical with the molecular conductivity.

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the values for K_0 calculated in this way show greater variation from the mean than do the values for μ_∞, they show no decided trend either to rize or to fall and may therefore be looked upon as constant. No such closeness of agreement is to be looked for in the values of K_0, since all of the errors in the calculation of μ_∞ are duplicated in that of K_0. Thus an error of 0.1 per cent. in the value for μ_v can result in one of 3 per cent. in K_0.

From the constancy of the values for μ_∞ calculated according to the dilution law, we may therefore conclude[1] that the dissociation of the substance in these solutions *obeys the law of mass action, although the electrolyte in question is as highly ionized as are the strong acids, bases and salts in aqueous solutions.* Whether this very unusual result is characteristic of the behavior of bases in acid solvents, or whether those substances which obey the law in one solvent obey it in all, irrespective of the degree of ionization, is a matter for further study. To decide this question, solutions of both strong and weak bases in formic acid will be investigated.

There is a slight possibility that, on account of the uncertainty in regard to the value to be used for the specific conductivity of the solvent, these results may prove to be accidental. This is rendered highly improbable, however, by the excellent agreement between the value for μ_∞ calculated as described above and that calculated in another way. That a simple relationship exists between the conductivities, at infinit dilution, of the same substance in different solvents and the viscosities of the solvents has been pointed out by a number of writers. A number of different formulas have been suggested,[2] but for our purposes the one expressing a simple inverse relationship will be sufficiently accurate. The electrolyte in the solutions of ammonia in formic acid is undoubtedly ammonium formate. The value of μ_∞ for this substance in water at 25° is 128.8, as calculated from the mobilities of the ions. The viscosity of water at this temperature is 0.009,[3] that of the acid is 0.0162.[4] Then according to the relation suggested, μ_∞ in formic acid should be:

$$\mu_\infty = 0.009/0.0162 \times 128.8$$
$$= 71.57$$

This differs by only 0.4 per cent. from the value found from our conductivity measurements, namely 71.85. This excellent agreement is very strong evidence of the correctness of the interpretation given above

[1] For the concentrations, $N/2$–$N/60$.

[2] See, for instance, Jones, Lindsay and Carrol, *Z. physik. Chem.*, 56, 170. Walden, *Ibid.*, 55, 207. Pisarzhevskii and Karp, *Ibid.*, 63, 257. Washburn, THIS JOURNAL, 33, 1461. The more accurate formulas must take into consideration the solvation in the respective solvents.

[3] Castell-Evans, "Physico-Chemical Tables," Vol. II, 598.

[4] *Ibid.*, 609. The last place of decimals is rounded off.

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for the behavior of the ammonia solutions and discounts any doubts introduced by the large conductivity of the pure acid.

We see therefore that the basic substance, ammonia, forms a highly dissociated electrolyte in the acid solvent, formic acid. The degree of dissociation actually obtained is, as a matter of fact, extremely great; ammonium hydroxide in water is about 4 per cent. ionized in 0.01 normal solution; potassium hydroxide about 95 per cent. in the same solvent and at the same concentration; ammonia in formic acid is about 99 per cent. ionized at the same concentration.[1]

In order to determin whether the high conductivity of the formic acid used as solvent might be alone sufficient to account for the decrease in the molecular conductivity of the ammonia solutions, as described above, a similar series of measurements was carried out with ammonium chloride as the solute. Since the data served also to confirm some conclusions which were drawn from the results discussed in the previous pages, they are given below in Table II. The data in this table have the same significance as those in the first five columns of the first table. It will be seen that, although the specific conductivities observed in the case of the ammonium chloride solutions reach as low a value as the specific conductivities, which in the ammonia series correspond to falling values for the molecular conductivity, no such decrease is noticeable here. This may be taken as evidence in favor of the interpretation of the falling values given above.[2]

TABLE II.—CONDUCTIVITY OF NH_4Cl IN HCOOH AT 25°.

c.	κ.	μ.	μ'_∞. (Kohlrausch).	μ_∞. (Ostwald).
0.2500	0.00848	33.94	...	...
0.1250	0.00473	37.83	52.73	44.18
0.0625	0.00256	40.96	52.94	45.73
0.03125	0.001364	43.65	53.36	46.17
0.01562	0.000715	45.75	53.52	47.28
0.00781	0.000384	49.16	53.69	50.22
0.00391	0.000197	50.59	56.09	51.10

Although the measurements, the results of which are given in the first two columns of Table II, were not as accurate as those for the ammonia solutions and must therefore not be considered as final, a brief discussion will not be out of place. It will be seen that neither the dilution law nor

[1] Although the electrolyte is ammonium formate, it must, in the acid solvent, be considered a base, as will be shown below.

[2] See p. 1928. The objection might be raised that in the ammonium chloride solutions a similar falling off in conductivity may be masked by a very great rise in the real molecular conductivities, *i. e.*, the conductivity of the acid may decrease what really is a much greater rise in these values than the one actually observed. This, however, is very improbable, since the rise in the molecular conductivity, as shown in the table, is very large for such dilute solutions and a more rapid increase would be most unusual.

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the equation of Kohlrausch give constant values for the conductivity at infinit dilution; in other words neither of these equations represents the course of the dissociation of the salt in the solutions. This is in agreement with similar findings of Zanninovich-Tessarin.[1] It is furthermore exactly what is to be expected when the nature of the salt is considered. For, in formic acid solution, *ammonium chloride is the salt of a strong base, ammonia (ammonium formate), and the very weak acid hydrogen chloride.*[2] *Consequently it should be partly decomposed by the solvent into these two substances, exactly as similarly constituted salts are hydrolyzed*[3] *in aqueous solutions.* Since the extent of this decomposition must vary with the concentration of the solution, none of the "dilution laws" could be expected to apply. That this interpretation is correct can be shown qualitatively by a simple experiment. If dried air is passed through the solution and then into water, the latter in a few moments gives a heavy precipitate of silver chloride with silver nitrate, showing that free hydrochloric acid is present in the solution of ammonium chloride in formic acid.[4] Similar experiments were carried out with formic acid solutions of potassium and sodium chlorides, and with potassium bromide and iodide. Corresponding results were obtained.[5] In fact, if all acids are but slightly ionized in formic acid, we might expect a similar behavior of all true salts in this solvent. Further interesting confirmation of these conclusions might be found by a comparison of the temperature coefficient of salts in formic acid with that of bases.[6]

[1] *Loc. cit.*

[2] See p. 1925.

[3] Similar analogies, for other solvents, have been pointed out by Franklin, THIS JOURNAL, 27, 820. Walden, *Z. physik. Chem.*, 54, 146. Ley, *Ibid.*, 30, 202. Bruni and Manuelli, *Z. Elektrochem.*, 11, 554.

[4] The addition of relatively small amounts of water, prevented the decomposition completely.

[5] Except that in the case of the iodide, hydrogen had to be used in place of air to prevent oxidation. The results were obtained most rapidly with the chloride and the least rapidly with the iodide. An attempt will be made to determin the equilibrium quantitatively by a modification of these experiments, or by some other method depending upon the partition principle, as may prove best. The conductivity of the salts, in the presence of an excess of the acids, will also be determined.

[6] In a recent article Prof. Garner has announced his intention of studying the conductivity, etc., of salts in formic acid solution (*Am. Chem. J.*, 46, 236 (1911)). The work described here was of course completed before the other appeared, and was begun long before Prof. Garner's intentions were known to the authors. Although our work is in no sense an infringement of the large field reserved by Prof. Garner, we shall make all efforts to avoid duplication of his work. We shall therefore not take up the study of temperature coefficients as suggested above, except for ammonium chloride to verify the conclusions which we drew from the main portion of our work (the study of bases in this solvent), nor shall we study the conductivity of salts, except of those which according to the views above presented, must, in formic acid solution, be considered as being analogous to bases in aqueous solutions, namely, the formates.

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Summary.

It has been shown:

(1) That the solutions obtained by dissolving ammonia in (anhydrous), formic acid are excellent conductors.

(2) That the substance formed in these solutions (ammonium formate), although a very highly ionized electrolyte, obeys the law of mass action (in the more concentrated solutions).

(3) That, in accordance with the conception that the salts of the halogens are in formic acid solution really the salts of strong bases (the formates) and of weak acids, potassium chloride, bromide and iodide and sodium and ammonium chlorides are decomposed by "formic acid hydrolysis."

Further work along the lines suggested is in progress, using formic acid as well as other acidic and basic solvents.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

EQUILIBRIUM IN THE SYSTEM, POTASSIUM IODIDE, IODINE AND WATER.

BY CHARLES L. PARSONS AND C. F. WHITTEMORE.

Received October 12, 1911.

The question of the existence of polyiodides of potassium has been for years one of deep interest to physical chemists, involving as it does so many theoretical questions. In July, 1910,[1] one of us in collaboration with H. P. Corliss, presented a paper at the San Francisco meeting of the American Chemical Society, attacking the problem through phase rule considerations in aqueous alcohol solutions. Experimental difficulties had previously made accurate work in aqueous solutions impossible in our hands, owing to the high specific gravity and great concentration. Aqueous alcohol was chosen in the expectation that more dilute solutions would result. Such, however, did not prove to be the case, but the experimental difficulties were overcome and the experience then gained seemed to make it desirable to study the mutual solubility of potassium iodide and iodine in pure water with special reference to that portion of the curve representing complete saturation, which had never before been plotted.

In describing the results it is unnecessary to refer again to the literature of the subject, which will be found in the article above mentioned, or indeed to describe methods of procedure or of analysis, for they were precisely the same as those previously used. The portion of the curve covered by dilute solutions was also not studied, as it has been carefully covered by Noyes and Seidensticker[2] and others.

[1] THIS JOURNAL, 32, 1367.

[2] *Z. physik. Chem.*, 27, 357 (1898).

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The bottles carrying solutions of varying concentration were placed in the thermostat in the late fall of 1910 and were rotated under water kept at 25° until equilibrium was shown to have been reached. During the early stages the bottles were examined every few days and more iodide or iodine added as the case might require, if the solid phase had all disappeared.

The results follow:

TABLE I.—THE MUTUAL SOLUBILITY OF IODINE AND POTASSIUM IODIDE IN WATER.

Serial No.	Sp. gr.	Analysis of liquid phase. Per cent. KI.	Analysis of liquid phase. Per cent. I.	Analysis of solid phase with adhering mother liquor. Per cent. KI	Analysis of solid phase with adhering mother liquor. Per cent. I.	Date of anal. 1911.
		(a) In equilibrium with excess of KI.				
1.....	1.733	60.39	0.0	KI	0.0	Apr. 4
		60.39	0.0	KI	0.0	Apr. 11
2.....	1.888	54.34	11.66			Mar. 24
		54.49	11.60	84.92	4.05	Apr. 1
3.....	2.066	49.04	23.06			May 20
		49.05	23.11	85.94	6.32	May 27
4.....	2.216	44.90	31.01			Mar. 27
		44.74		80.46	10.84	Apr. 29
5.....	2.539	38.04	44.54			Mar. 27
		38.09	44.58	78.56	15.23	Apr. 30
6.....	2.560	37.71	45.54			Feb. 27
		37.60	45.56	77.32	16.73	Mar. 30
7.....	2.665	35.77	49.65			May 18
		35.84	49.57			June 1
8.....	3.232	29.65				Apr. 5
		29.77	62.81	39.99	56.10	Apr. 11
9.....	3.246	27.98	66.42			May 21
		27.86	66.48	38.78	56.27	June 1
		(b) In equilibrium with excess of I.				
11.....	1.349	15.99	18.51			June 1
		16.06	18.47	3.04	85.43	May 8
12.....	1.516	19.77	26.11			May 24
		19.64	26.21	4.48	83.87	May 30
13.....	1.769	22.84	36.04			May 18
		22.92	36.08	3.70	89.33	June 2
14.....	1.910	23.64	40.52			Mar. 8
		23.46	40.51	6.49	83.62	Apr. 3
15.....	2.403	24.73	53.62			Mar. 6
		24.83	53.59	8.62	83.81	May 11
16.....	2.904	24.90	63.11			Mar. 9
		25.09	63.14	4.82	92.41	Apr. 28
17.....	3.082	25.28	66.10			Mar. 14
		25.08	65.98	4.00	94.39	Apr. 25
		(c) Invariant point. Excess of KI and I.				
18.....	3.316	26.05	68.06			May 12
		25.96	68.01	16.14	83.77	May 17
		26.04	68.16			May 22
		25.92	68.13	11.32	86.56	May 30

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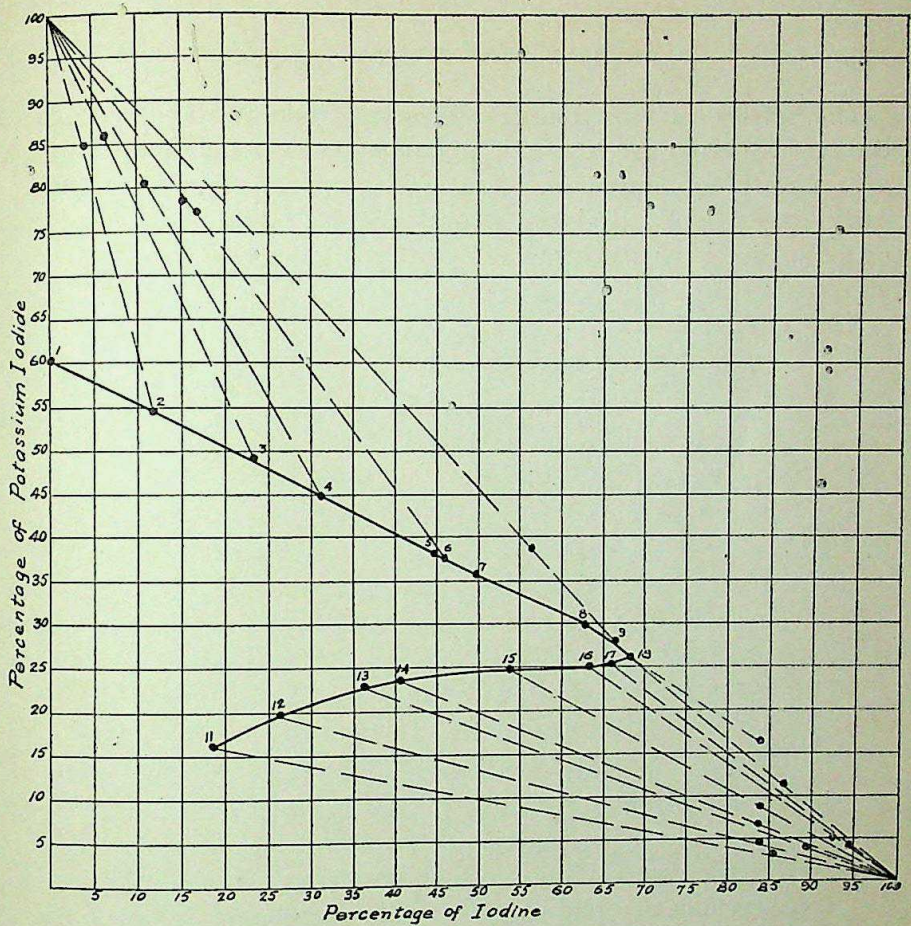

Fig. 1.

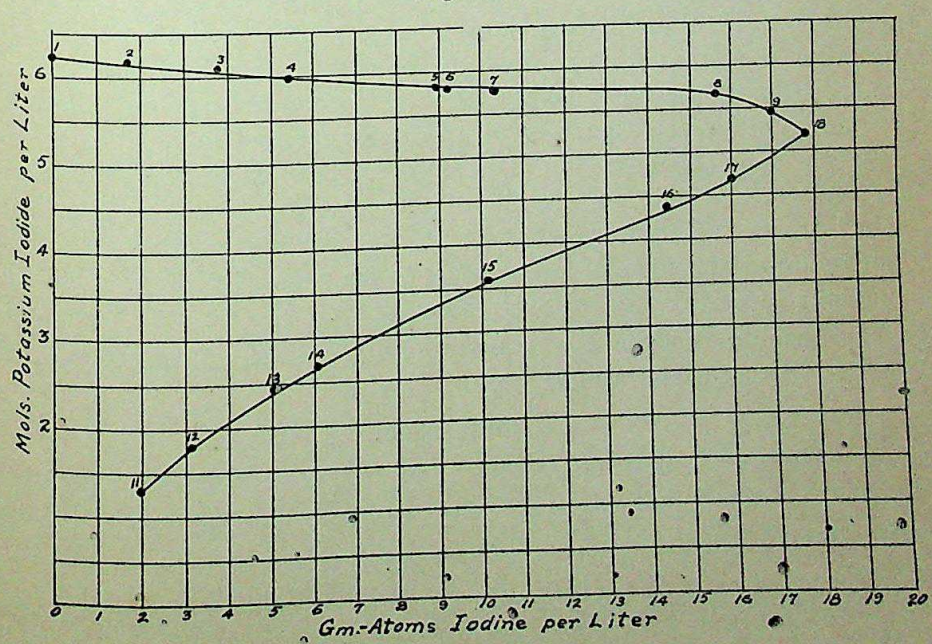

Fig. 2.

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The preceding data recalculated to moles KI and grams atoms of I per liter of solution gave the following results:

Serial No.	KI moles.	I g. atoms.
1	6.23	0.00
2	6.19	1.72
3	6.10	3.77
4	5.97	5.41
5	5.82	8.91
6	5.79	9.18
7	5.73	10.30
8	5.67	15.64
9	5.44	17.00
10	0.00	0.00
11	1.30	1.96
12	1.79	3.13
13	2.44	5.02
14	2.69	6.09
15	3.59	10.15
16	4.38	14.45
17	4.66	16.03
18	5.17	17.80

As water does not enter into the composition of the solid phase but acts simply as a solvent, it is possible to plot the results on an ordinary two-axis diagram, and the prolongation of the lines drawn through the points representing the composition of the liquid phases and those representing the composition of the solid phase with adhering mother liquor in equilibrium therewith will meet at a point representing the composition of the solid phase, if the solid phase is simply one of the components. In the following diagram (Fig. 1), in which the numbered points represent the composition of the liquid phases and the unnumbered points the corresponding solid phases together with adhering mother liquor, it is at once apparent that the only solid phases present throughout the whole series are potassium iodide on one side of the curve and iodine on the other. The invariant point 18 was shown to be in equilibrium with iodine alone, potassium iodide alone, or any mixture of the two and is therefore the one and only invariant point in the system at 25°.

The compositions of the solutions for the sake of convenience are plotted in another form in Fig. 2.

Conclusion.

While these results must follow if the previous work of Parsons and Corliss[1] is correct, they again prove conclusively that no solid polyiodide of potassium exists at 25°.

DURHAM, N. H.

[1] THIS JOURNAL, 32, 1367.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE SOLUBILITY OF SILVER CHLORIDE IN CHLORIDE SOLUTIONS AND THE EXISTENCE OF COMPLEX ARGENTICHLORIDE IONS.

BY GEORGE SHANNON FORBES.

Received October 9, 1911.

It has long been known that silver chloride is fairly soluble in concentrated solutions of various chlorides. Reinsch[1] speaks of its solubility in concentrated hydrochloric acid. Vogel,[2] who appears to have made the first quantitative study of the reaction, gives solubilities in acid of specific gravity 1.165 to which varying proportions of water had been added, and also speaks of the increase of solubility with the temperature. Mulder[3] studies its solubility qualitatively in other chlorides. These and other references to early work on the subject are found in Comey's "Dictionary of Solubilities," pages 372–3. The only attempt to find numerical regularities seems to have been made by Barlow[4] who, while seeking errors in a method for determining sulfur, titrated solutions of sodium chloride, or of hydrochloric acid, or of both together, with silver nitrate. He concludes: "The figures show that the solubility of sodium chloride falls off (at a gradually diminishing rate) with diminishing concentration." He investigated only one concentration of hydrochloric acid. The solubilities as observed by Barlow appear roughly proportional to the concentration of sodium chloride. Noyes and Bray,[5] perhaps with these figures in mind, stated that a complex anion like $AgCl_2'$ probably exists in such solutions.

Researches concerning reactions between other pairs of halides are numerous. Of those most closely related to the present research may be mentioned that by Hellwig,[6] who prepared in solid form many complex compounds of silver halides with silver nitrate, also with alkali halides including thiocyanates. He failed to isolate a complex salt between silver chloride and other chlorides, and did not study the reaction further. This field was next investigated by Bodländer,[7] who found evidence of complex anions of the type AgX_4, and by Krym,[8] who dealt with the iodides of sodium and silver. Important work on halides of mercury and copper will be referred to in the discussion of results below.

The theory of such complex compounds has been discussed at length by Abegg.[9]

[1] *J. prakt. Chem.*, 13, 133.
[2] *N. Rep. Pharm.*, 23, 355.
[3] *Loc. cit.*
[4] THIS JOURNAL, 28, 1446 (1906).
[5] *Ibid.*, 29, 166 (1907).
[6] *Z. anorg. Chem.*, 25, 157 (1900).
[7] *Ber.*, 36, 2878 (1903).
[8] *J. Russ. Phys. Chem. Ges.*, 41, 382 (1909); abstracted in *Chem. Zentr.*, 1909, II, 681.
[9] *Z. anorg. Chem.*, 20, 453–499 (1899).

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The present research aimed to determin the solubility of silver chloride in a large variety of aqueous chloride solutions; to find what complex ions, if any, were indicated by the data, and to draw conclusions if possible regarding the relative "activities"[1] of the chloride ion in such solutions.

Very concentrated indeterminate solutions of the chlorides were prepared and carefully filtered. The ammonium chloride was barely acidified with hydrochloric acid to avoid hydrolysis. The purity of the materials is discussed below after recording the effect of impurities intentionally introduced. Silver chloride was precipitated from weighed portions diluted with much water and weighed on platinum Gooch crucibles with the usual precautions. Dilute solutions of silver nitrate, one about hundredth normal, the other about quarter normal, also one of silver sulfate for use with hydrochloric acid, about fortieth normal, were made and analyzed with equal care.

The determinations were carried out in flat-bottomed glass cylinders of about 60 cc. capacity, except in the case of the most dilute solutions, where deep beakers holding 600 cc. were used. These were set on a porcelain plate covered with black glazed paper and immersed to a suitable depth in a thermostat electrically regulated to maintain a temperature (corrected) of 25.06° within a few hundredths of a degree. The solutions were examined for opalescence in horizontal light reflected by an immersed forty-five degree mirror from an incandescent lamp supported above the thermostat.

The method was as follows: The dry cylinder was counterpoised, then carefully weighed with a convenient amount of chloride solution. Water, or in some cases the solid salt, was added and the additional weight found as before. A silver solution was next run in from a weight buret until equilibrium was nearly reached at some temperature between 24° and 26°. The vessel was then immersed in the thermostat and ten minutes allowed for the final adjustment of temperature—ample time, as proved by special experiments. Hundredth normal silver nitrate was added drop by drop until the faintest opalescence visible persisted after careful stirring. Immediately after the final adjustment the cylinder was wiped and weighed with the stirrer. Then the true density was determined within one part in five thousand by a pycnometer. All effects of evaporation or change of volume on mixing were thus avoided.

The above end point was proved sufficiently near the true equilibrium by the following considerations: Concentrated chloride solutions nearly saturated with silver chloride show a surprizing degree of supersaturation on cooling; this can be promptly relieved by adding, on the end of a stirring rod, quantities of precipitated silver chloride so minute as to produce no visible turbidity in 50 cc. of pure water. In such concentrated

[1] Lewis, *Proc. Am. Acad.*, 43, 288 (1907).

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chlorides the precipitation of silver chloride is very prompt; larger quantities of it are required to produce visible opalescence in these solutions than in very dilute ones. The precipitate looks coarser from the start, and becomes rapidly more so, therefore it should not be allowed to stand more than a few minutes. Various chloride solutions at 25° were treated with successive drops of hundredth normal silver nitrate, seeding after each drop with minute portions of silver chloride. This seeding never produced any effect in solutions which had been cleared by stirring, hence such solutions were not supersaturated. If the last drop of silver nitrate produced a permanent precipitate, this was dissolved by heat and the solution quickly cooled to 25°, after which seeding *always* produced a precipitate. These experiments eliminated the danger that solutions which had failed to dissolve all the silver chloride formed in them were unsaturated, for if this had been the case, no precipitate would have been produced on seeding at 25° after cooling. Thus it was proved that the solutions at 25°, in which the faintest cloud remained, were saturated, and that the excess hardly exceeded that derived from the last drop. Such an excess in 50 cc. was equivalent to 6×10^{-6} mole per liter, the maximum probable error in the silver concentrations given below.

After much consideration it was decided to record all concentrations in gram equivalents per liter. As ample evidence was available that the chloride ion was the active agent, it seemed that the cations and the undissociated molecules with their possible hydrate water might well count as free space. Concentrations could hardly be calculated on such a basis for lack of any means of determining the volume occupied by the chlorine ion. Trial calculations showed that the conclusions drawn from the following figures would be substantially unchanged if concentrations were reckoned in equivalents per thousand grams of water. The table gives the total concentration of dissolved silver, and of the chloride in each case, the symbols being [Ag] and [MCl] where M is a gram equivalent of any metal. $K_m = [Ag]/[MCl]^m$ where m is a small whole number:

TABLE I.

Sodium Chloride.

$[Ag] \times 10^3$.	[NaCl].	$k_2 \times 10^4$.	$k_3 \times 10^4$.
0.086	0.933	0.98	1.05
0.130	1.190	0.92	0.77
0.184	1.433	0.90	0.63
0.245	1.617	0.94	0.58
0.348	1.871	0.99	0.53
0.446	2.094	1.04	0.50
0.570	2.272	1.10	0.486
0.684	2.449	1.14	0.466
0.851	2.658	1.20	0.453
1.040	2.841	1.29	0.453

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TABLE I (*continued*).

Sodium Chloride.

$[Ag] \times 10^3$.	[NaCl].	$k_2 \times 10^4$.	$k_3 \times 10^4$.
1.194	3.000	1.33	0.442
1.583	3.270	1.48	0.453
1.897	3.471	1.57	0.454
2.462	3.747	1.75	0.468
2.879	3.977	1.82	0.458
3.335	4.170	1.92	0.460
3.810	4.363	2.05	0.458
4.298	4.535	2.09	0.461
6.039	5.039	2.38	0.472

Calcium Chloride.

$[Ag] \times 10^3$.	$[CaCl_2/2]$.	$k_2 \times 10^4$.	$k_3 \times 10^4$.
0.289	1.748	0.95	0.54
0.501	2.201	1.03	0.47
0.900	2.741	1.20	0.44
1.463	3.264	1.37	0.42
2.182	3.737	1.56	0.418
2.802	4.033	1.72	0.427
4.175	4.538	2.03	0.447
5.823	5.005	2.32	0.464

Ammonium Chloride.

$[Ag] \times 10^3$.	$[NH_4Cl]$.	$k_2 \times 10^4$.	$k_3 \times 10^4$.	$k_4 \times 10^4$.
0.042	0.513	1.59	2.46	...
0.113	0.926	1.33	1.43	...
0.172	1.141	1.32	1.16	...
0.365	1.574	1.47	0.94	...
0.842	2.143	1.80	0.86	...
1.425	2.566	2.16	0.84	...
2.160	2.918	2.54	0.87	...
2.795	3.162	....	0.88	0.280
4.029	3.510	....	0.93	0.265
9.353	4.363	....	1.13	0.258
14.92	4.902	....	1.27	0.258
24.04	5.503	....	1.44	0.262
30.17	5.764	....	1.57	0.273

Strontium Chloride.

$[Ag] \times 10^3$.	$[SnCl_2/2]$.	$k_2 \times 10^4$.	$k_3 \times 10^4$.	$k_4 \times 10^4$.
0.033	0.550	1.10	2.00	...
0.092	0.989	0.94	0.95	...
0.173	1.359	0.94	0.69	...
0.236	1.572	0.95	0.61	...
0.284	1.698	0.98	0.58	...
0.348	1.818	1.05	0.58	...
0.510	2.140	1.11	0.52	...
0.747	2.476	1.22	0.49	...
1.252	2.992	1.40	0.47	...
2.018	3.494	1.65	0.47	...
3.594	4.152	2.08	0.50	0.121
8.174	5.216	3.00	0.58	0.110
12.04	5.775	3.61	0.62	0.108

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TABLE I (*continued*).

Potassium Chloride.

$[Ag \times 10^3]$.	[KCl].	$k_2 \times 10^4$.	$k_3 \times 10^4$.	$k_4 \times 10^4$.
0.141	1.111	1.11	1.03	...
0.235	1.425	1.16	0.81	...
0.391	1.713	1.33	0.78	...
0.616	2.022	1.51	0.74	...
1.050	2.396	1.84	0.763	...
1.390	2.628	....	0.766	0.291
1.845	2.850	....	0.797	0.280
2.435	3.081	....	0.83	0.270
3.602	3.424	....	0.90	0.262
5.725	3.843	....	1.01	0.262

Hydrochloric Acid.

$[Ag \times 10^3]$.	[HCl].	$k_2 \times 10^4$.	$k_3 \times 10^4$.
0.032	0.649	0.76	1.18
0.126	1.300	0.75	0.57
0.266	1.911	0.73	0.38
0.374	2.149	0.81	0.38
0.610	2.569	0.86	0.325
0.814	2.975	0.92	0.309
1.358	3.576	1.06	0.297
2.147	4.182	1.23	0.294
3.168	4.735	1.41	0.298
5.126	5.508	1.69	0.307

Barium Chloride

$[Ag] \times 10^3$.	$BaCl_2/2$.	$k_2 \times 10^4$.	$k_3 \times 10^4$.
0.186	1.248	1.20	0.96
0.339	1.610	1.31	0.81
1.274	2.676	1.78	0.67
2.366	3.260	2.20	0.67

Since silver chloride is virtually insoluble in concentrated mercuric chloride solution, the chloride ion, and not the undissociated molecules, must be responsible for its solubility in the cases studied above. In the rather feebly dissociated zinc chloride its solubility is small, 0.000364 mole per liter of 4.777 normal solution as compared with 0.0135 mole in ammonium chloride equally concentrated. Richards and Archibald[1] found mercurous chloride unchanged by concentrated cadmium chloride solutions, although highly dissociated chlorides decomposed it into mercuric chloride and mercury. They similarly attributed the lack of action to the low concentration of the chloride ion.

Bodländer and Storbeck[2] proved very conclusively that the complex anion $CuBr_2'$ is present in a solution of cuprous bromide in potassium bromide. Richards and Archibald[2] concluded that the ion $HgCl_4''$ was

[1] *Proc. Am Acad.*, 37, 347 (1902).
[2] *Z. anorg. Chem.*, 31, 1 (1902).

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formed according to the reaction $Hg_2Cl_2 + 2Cl' \rightleftharpoons HgCl_4'' + Hg$. The results presented above are now completely explained by assuming the existence of complex anions of the type $(AgCl)_xCl^{n'}$, where x is probably one by analogy with the very similar cuprous bromide. If $AgCl + mCl' \rightleftharpoons AgCl_{m+1}^{m'}$, then according to the so-called law of mass action, if this may be assumed to hold in spite of the high concentration, $[Ag] = k[Cl']^m$ in a solution saturated with silver chloride. If next the further assumption is made, as no better could be devized, that the activity of the chloride ion is nearly proportional to the total chloride concentration throughout moderate ranges of the latter, the figures in Table I may be explained. The values of k_2, in the third column, are constant from $1.5n$ down to the smallest concentrations studied; that is, solubility is closely proportional to the square of the chloride concentration. Support is thus lent to the hypothesis that the ion $AgCl_3''$ exists in such solutions. No evidence of the ion $AgCl_2'$ is to be found.[1] In the fourth column the values of k_3 are very constant from $2.5n$ upward, that is, solubility is closely proportional to the cubes of the concentrations, hence the ion $AgCl_4'''$ is suggested, except in the cases of potassium and ammonium chlorides, where this ion appears to be present from $1.5n$ to $3.0n$, above even which a third ion, $AgCl_5''''$, is suspected from the data.

That m is really integral throughout considerable ranges of concentration, and does not increase continuously except in those solutions where no single complex predominates, is also shown by plotting the common logarithms of the chloride concentrations as abscissas against the common logarithms of the silver concentrations as ordinates. The equation of any graph is found by taking the logarithm of each side of the equation $[Ag] = km[MCl]^m$ for the corresponding salt. The result is: $\log [Ag] = \log km + m \log [MCl]$, which is the equation of a straight line if m is a constant. Now all the graphs are seen to consist of straight parallel lines connected by shorter curved portions, which shows that m is constant and also the same for different salts throughout given ranges of concentration. The values of $\frac{\Delta \log [Ag]}{\Delta \log [MCl]}$, which must be numerically equal to m, are seen to be almost exactly equal to 2, 3 or 4, according to the concentration region in which the straight lines lie. Thus it is shown graphically that complex ions of silver chloride molecules with two, three or perhaps even four chlorine ions exist in well defined concentration intervals.

Is it possible to connect the solubility of silver chloride more closely with the true concentration of the chloride ion? Not only is the latter uncertain, but also the degree of association of the complex anions with

[1] The increase in k_2 at the smallest concentrations is to be attributed largely to the excess of silver chloride used to produce opalescence.

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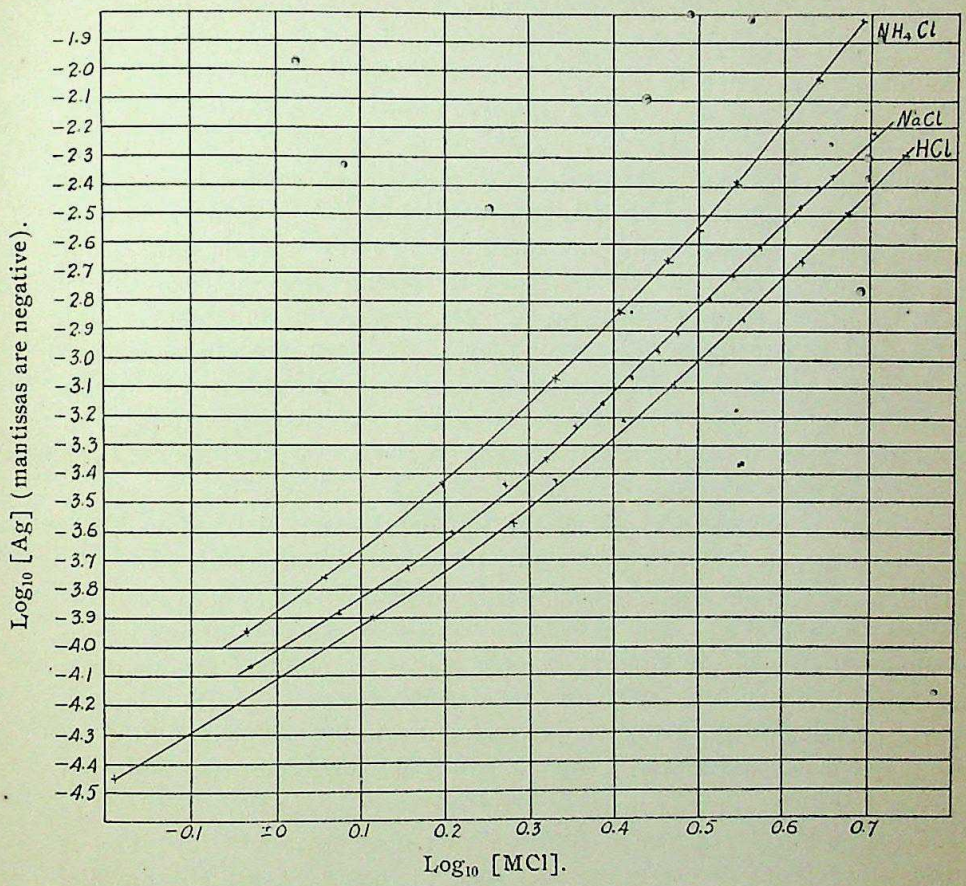
cations is entirely unknown. The work of Le Blanc and Noyes[1] on the conductance and catalytic power of hydrochloric acid containing mercuric chloride, and the experiments of Richards and Archibald[2] on the



conductance of sodium chloride containing mercuric chloride led them to conclude that any well dissociated chloride, MCl, and the complex compound M_2HgCl_4 are about equally dissociated up to normal concentration of the former. Thus the total mercury could be written as $C+C(1-\alpha)/\alpha$ or C/α, where C represented the concentration of the ionized portion. Then by the law of mass action $C/\alpha = k\,x^m/\alpha$, where x is the specific conductance of chloride and m the number of chloride ions entering the complex. To find whether a corresponding relation existed in the case of silver chloride, sodium nitrate was added to sodium chloride solution before running in silver solution. If in the case of the silver complex we can write $C/\alpha = k\,x^m/\alpha$, any repression of ionization should *lower* the total solubility, since the complex ion must decrease as the mth power of the

[1] Le Blanc and Noyes, *Z. physik. Chem.*, 6, 389, et seq. (1890).

[2] *Proc. Am. Acad.*, 37, 347 (1902).

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chloride ion, while the associated part increases only as the first power of the same. Consider now Table II; the k' values are interpolated for equal concentrations of pure chloride:

TABLE II.

$[Ag] \times 10^3$.	[NaCl].	$[NaNO_3]$.	$k_2 \times 10^4$.	$k_3 \times 10^4$.	$k_2' \times 10^4$.	$k_3' \times 10^4$.
2.457	3.743	0.00	1.75	0.469	....	...
2.493	3.592	0.84	1.93	0.538	1.65	0.461
2.538	3.462	1.50	2.12	0.611	1.57	0.454

The addition of sodium ion increases the constants, and hence the solubility also. Neglecting the change in the medium produced by so much sodium nitrate, it would appear that the concentration of at least the trivalent anion $AgCl_4'''$ is lowered relatively much more than that of the chloride ion by adding sodium ion, for the increase in $[M_3AgCl_4]$ far more than compensates for the loss in $[AgCl_4''']$. Therefore the hypothesis of equal dissociation of MCl and M_3AgCl_4 was abandoned, and in despair of evaluating the many unknown variables, the activity of the chloride ion was taken as roughly proportional to total chloride concentration for moderate increments of the latter.

Richards and Archibald[1] suggested that the extent of action of chlorides on mercurous chloride might possibly be used to determin the concentration of the chloride ion. If the extent of action in the case of each such complex is an explicit function of the activity of the chloride ion, a mere comparison of constants ought to show whether complex formation is a measure of the relative activities in various solutions. In normal solutions, where the same type of complex ion is formed from both mercuric and silver chlorides, k_2 may be calculated from the data of Richards and Archibald, $k_2 = \frac{[Hg] \text{ dissolved}}{[MCl]^2}$.

	HCl.	NaCl.	$CaCl_2$.	$BaCl_2$.
$k_2 \times 10^4$ for $HgCl_2$.....	2.4	2.0	1.7	2.2
$k_2 \times 10^4$ for $AgCl_2$.....	0.75	0.97	0.9	1.2

The ratio between the hydrochloric acid constants differs so widely from the other ratios that the difference cannot be attributed to errors in experiment or extrapolation. Redistillation of the acid failed to increase the values of its constants. It must therefore be concluded that complex formation by mercurous and silver chlorides is not proportional to the activity of the chloride ion unless perhaps a single salt is considered at a time. Possibly the undissociated portions of the chlorides, while incapable of direct combination with silver chloride, support or hinder the action of the chloride ion in varying degrees.

One equilibrium was determined in the presence of a known amount of sodium bromide:

[1] *Proc. Am. Acad.*, 37, 359 (1902).

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$[Ag] \times 10^3$.	$[CaCl_2/2]$.	[NaBr].	$k_2 \times 10^4$.	$k_3 \times 10^4$.	$k_2' \times 10^4$.	$k_3' \times 10^4$.
5.62	5.074	0.0018	2.18	0.430	2.37	0.467

These figures, together with those on sodium nitrate, show pretty conclusively that the purest commercial preparations, such as were used in this research, could hardly have contained impurities of serious consequence to the results. Bromide and iodide were the only anions capable of forming highly insoluble silver compounds which were likely to be present. No test for these could be obtained, and yet a fifth of the above concentration of bromide can be detected under the same conditions with carbon disulfide and chlorine water. Of other salts it appeared likely, in view of the results with sodium nitrate, that even a whole per cent. would have had a negligible effect.

The temperature coefficient of the solubility was investigated in thrice normal potassium and calcium chlorides, salts widely different in most respects, at 1.0°, 25.0° and 35.0°. Silver nitrate was first introduced at 1.0° until equilibrium was attained; then the solution was warmed to 25.0° and more silver nitrate added; then a further addition was made at 35.0°. The normality of the chloride was changed by each addition of silver solution, so that in order to compare solubilities at the *same* concentration but at different temperatures extrapolation was necessary. Table I shows that for these concentrations $[Ag]/[KCl]^4 = k_4$ and $[Ag]/[CaCl_2/2]^3 = k_3$ at 25.0°. Assuming these equations to hold at 1.0° and 35.0°, take the logarithm of each side and differentiate. $\Delta \log [Ag] = 4\Delta \log [KCl]$ and $\Delta \log Ag = 3\Delta \log [CaCl_2/2]$. The solubilities in 3.083*n* KCl and in 3.320*n* $CaCl_2$ may now be calculated at 1.0° and 35.0°. The "primes" indicate values obtained with the help of this artifice.

t.	$[Ag] \times 10^3$.	[KCl].	$[Ag]' \times 10^3$.	[KCl]'.	$\log[Ag]'_{t_2} - \log[Ag']_{t_1}$.	$\frac{\log[Ag]'_{t_2} - \log[Ag]'_{t_1}}{t_2 - t_1}$.
1.0°	1.734	3.325	1.283	3.083		
					0.2747	0.0113
25.0°	2.415	3.083	2.415	3.083		
					0.1356	0.0136
35.0°	2.786	2.955	3.300	3.083		

t.	$[Ag] \times 10^3$.	$[CaCl_2/2]$.	$[Ag]' \times 10^3$.	$[CaCl_2/2]'$.	$\Delta \log [Ag]'$.	$\Delta \log [Ag]'/\Delta t$.
1.0°	0.964	3.512	0.814	3.320		
					0.2694	0.0112
25.0°	1.514	3.320	1.514	3.320		
					0.1156	0.0116
35.0°	1.806	3.221	1.976	3.320		

The increase in solubility with temperature is roughly logarithmic, about three per cent. change for one degree, hence the variations of a few hundredths of a degree were permissible in the determinations. The activity of the chloride ion seems to vary with temperature to about the

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same extent in both salts, the differences being perhaps due to unequal changes in dissociation with temperature.

The data obtained in the research incidentally make it possible to calculate what excess of chloride will make silver chloride most insoluble—an imporant question in analytical work. As the solubility product of silver chloride at 25° is nearly 2×10^{-10},[1] the concentration of silver in solution due to incomplete repression of ionization is given by the equation $[Ag]_1 = 2 \times 10^{-10}/[MCl]$, assuming complete dissociation of MCl. The concentration of silver in solution due to complex ion formation is given by the equation $[Ag]_2 = 10^{-4}\ [MCl]^2$, where 10^{-4} is the average value of k_2 at low concentrations. Total dissolved silver is the sum of the above: $[Ag] = 2 \times 10^{-10}/[MCl] + 10^{-4}\ [MCl]^2$. Differentiating, $d[Ag]/d[MCl] = -2 \times 10^{-10}/[MCl]^2 + 2 \times 10^{-4}\ [MCl]$. If the left hand side of the equation becomes zero, $2 \times 10^{-10}/[MCl]^2 = 2 \times 10^{-4}\ [MCl]$ whence $[MCl] = 10^{-4}$. Hence silver chloride ought to be most insoluble in hundredth normal chloride solutions.

One determination was also made of the solubility of silver chloride in concentrated silver nitrate.[2] This salt was recrystallized from fifty per cent. nitric acid, whirled on a centrifugal, fused in a platinum dish, and dissolved to form a solution about twice normal. A cloud was produced in 40 cc. by 0.09 cc. of 0.014 *N* KCl, that is, by a concentration of 3×10^{-5} gram equivalent or 0.001 gram of chlorine per liter, less than one-tenth the solubility of silver chloride in a twice normal chloride solution.

Summary.

The solubility of silver chloride in concentrated solutions of various chlorides was determined mainly at 25°.

The solubility is nearly doubled in going from 0° to 25°, the rate of increase above and below 25° being nearly logarithmic.

The solubility is sharply proportional to integral powers of the chloride concentration throughout considerable ranges, a fact explained by assuming the existence of the complex anions $AgCl_3''$, $AgCl_4'''$ and possibly $AgCl_5''''$. No evidence of the ion $AgCl_2'$ is found.

The extent of complex formation by mercurous and silver chlorides cannot be used as a measure of the activity of the chloride ion in concentrated solutions.

Silver chloride should be most insoluble, at 25°, in hundredth normal chloride solutions.

CAMBRIDGE, MASS.

[1] Data from Goodwin, *Z. physik. Chem.*, 13, 645 (1894).

[2] Heflwig, *Z. anorg. Chem.*, 25, 177 (1900), states that 100 cc. of thrice normal silver nitrate dissolved 0.08 gram of silver chloride, a quantity which fell off *very* rapidly with dilution.

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[FROM THE PATHOLOGICAL DEPARTMENT OF ST. LUKE'S HOSPITAL, NEW YORK. F. C. WOOD, DIRECTOR.]

THE DETERMINATION OF COPPER—A MODIFICATION OF THE IODIDE METHOD.

By E. C. KENDALL.

Received October 21, 1911.

For the determination of copper the most important methods are the electrolytic, the iodide, and the cyanide. As the determination by means of the electrolytic method requires a considerable amount of time and apparatus, the only methods for the rapid estimation of copper are the iodide and the cyanide.

Upon an examination of the two volumetric methods mentioned it is apparent that in respect to the amount of time and attention required for a determination the cyanide has a great advantage over the iodide method. However, in respect to the accuracy of the results obtained the iodide method is conceded to be by far the more accurate of the two. As every consideration would be in favor of the iodide method if it could be modified in such a way as to make it as rapid and easy of manipulation as the cyanide method, an attempt was made to make such a modification.

In the determination of copper by the iodide method the copper may be originally present as copper, copper oxide, or sulfide. The first step is to obtain the copper in solution. Practically the only way to do this is to dissolve it in nitric acid. The solution of the copper with nitric acid produces nitrous acid in the solution, and it is the removal of this which causes the delay in the estimation of the copper. As the method is described in the literature, the nitrous acid is destroyed with bromine, the excess of bromine being removed by boiling; or the nitrous acid is removed by evaporating to dryness.

The modification of the iodide method as described in this paper consists in the destruction of the nitrous acid without boiling. This is accomplished by the addition of a small amount of sodium hypochlorite. The addition of sodium hypochlorite to a nitric acid solution produces hypochlorous acid. The interaction of hypochlorous acid and nitrous acid results in the oxidation of the nitrous acid and the formation of hydrochloric acid, and the reaction between hypochlorous and hydrochloric acid results in the destruction of the hypochlorous acid and the formation of free chlorine and water. As the solution of sodium hypochlorite contains small amounts of chlorides, hydrochloric acid will always be present when the solution is acidified, thus insuring the destruction of the hypochlorous acid and the formation of free chlorine. We thus see that the effect of adding sodium hypochlorite to the solution is the complete destruction of the nitrous acid and the formation of free chlorine.

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To remove the free chlorine in solution some compound must be added which will take up the chlorine, but will not affect subsequent operations. Such a compound is found in phenol. Under the conditions of the determination, phenol will add chlorine directly to the benzene ring, but is not affected by iodine or any of the other compounds in the solution. Chlorophenol not being ionized removes all traces of free chlorine.

This modification of the method greatly reduces the time and attention required for a determination, and, in addition, the copper solution is prepared in such a way that iodine can be liberated by copper alone.

In the determination, the copper, copper oxide, or sulfide is dissolved in nitric acid. After the addition of the sodium hypochlorite and phenol, which requires but a moment, the solution is made slightly alkaline with sodium hydroxide, and is then made acid with acetic acid, when the solution is ready for titration. Potassium iodide and starch are added, and the titration is made to the disappearance of the starch iodide color. There is never any fear of the blue color "flashing back," and the solutions will remain colorless indefinitly after the titration. As the ionization constant for acetic acid is too low to allow nitrates to liberate iodine, the amount of nitric acid in solution is immaterial. Even 20 cc. of concentrated nitric acid will not affect the titration. However, too great an acidity is to be avoided, as nitrophenol will be formed. The presence of nitrophenol prevents the determination of copper, but there is no danger of its formation even in the presence of a large amount of acid if the solution is neutralized soon after the addition of the phenol. If a large amount of nitric acid is used to dissolve the copper, it should therefore be partly neutralized before addition of the phenol.

As chlorine easily oxidizes phenol to compounds which prevent the determination of copper it is essential that all of the phenol be added quickly to the solution. Under these conditions the chlorine adds directly to the benzene ring, but if the phenol is added drop by drop the chlorine will oxidize it, producing colored compounds in solution.

In order to add the phenol quickly enough to the solution it may be poured in from a beaker, or, a more convenient way, from a pipet from which the tip has been removed so that the delivery is from an opening which is of the same bore as the rest of the tube. By forcing the phenol out of such a pipet with the breath the entire volume is added very quickly and at the same time the phenol is well mixed with the contents of the flask.

After addition of the phenol the chlorine gas which is in the flask above the liquid is removed by blowing it out with the breath, and the sides of the flask are washed with a jet of water from a wash bottle. There should be no odor of chlorine just before the solution is made alkaline.

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It should be remembered that the end point of the titration is not pure white. Cuprous iodide has a cream color, and when a large amount of copper is present the cuprous iodide gives a decided tint to the solution. When the end point is nearly reached a drop of the thiosulfate is allowed to fall into the center of the flask. If a change of color occurs the solution is given a slight rotary motion and after the solution is again quiet another drop of the thiosulfate is added. This "spot test" is easily recognized and gives a very accurate end point.

The speed of reaction of the copper with potassium iodide varies with the volume. In a small volume the action is rapid and all of the iodine is liberated at once, but in a large volume an appreciable time may be required for all of the copper to react. This is especially noticeable when a small amount of copper is present. A high concentration of potassium iodide greatly assists the liberation of the iodine. Accurate results can not be obtained unless at least 3 grams of potassium iodide are added, irrespective of the amount of copper present, up to 500 mg. of copper.

The solutions required are:[1]

A. *The Sodium Hypochlorite* solution is made by boiling together a mixture of 112 grams of calcium hypochlorite and 100 grams of anhydrous sodium carbonate in 1200 cc. of water. After the calcium is precipitated as carbonate, the solution is filtered and its strength found as follows: 5 cc. of the hypochlorite solution are added to 100 cc. of water containing 5 cc. of 30 per cent. potassium iodide solution, and a few cc. of dilute hydrochloric acid are added. The liberated iodine is titrated with 0.1 *N* sodium thiosulfate. The volume of the solution is now adjusted so that 5 cc. of the hypochlorite solution are equivalent to 30 cc. of 0.1 *N* sodium thiosulfate.

B. *Phenol.*—A 5 per cent. colorless solution of phenol.

C. *Sodium Hydroxide.*—A 20 per cent. solution.

D. *Acetic Acid*, 50 per cent.

E. *Potassium Iodide.*—A convenient way to use this is to prepare a solution which contains 30 grams per 100 cc. of solution. Then 10 cc. will contain 3 grams, which is the amount needed for a determination.

F. *Sodium Thiosulfate.*—For the accurate titration of the liberated iodine two solutions are used. One strong solution, 1 cc. of which equals 6 mg. of copper, and a weak solution, 1 cc. of which equals 1 mg. of copper. The strong solution is run in until the iodine liberated by the copper gives a light straw color to the solution. Starch is then added and the titration is finished with the weak solution.

[1] The weights given here are for calcium hypochlorite having 35 per cent. or more available chlorine.

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As a thiosulfate solution loses strength, it should be restandardized from time to time. A convenient way to do this is as follows: A solution of sodium thiosulfate, approximately 0.1 *N*, is made by dissolving 24 grams of the crystallized salt per liter of water. After the solution has stood at least twenty-four hours it is standardized against copper by the method described below. Pure electrolytic copper which has been cleaned with emery paper should be used. After dissolving 150 to 200 mg. of the copper in 6 to 8 cc. of 50 per cent. nitric acid the solution is treated as described below and the thiosulfate is then standardized with this known weight of copper. The most convenient means of restandardizing the thiosulfate is to use a solution of acid potassium iodate. Acid potassium iodate has the formula $KIO_3.HIO_3$, so that a normal solution has one-twelfth the molecular weight in grams per liter. A 0.1 *N* solution is prepared by dissolving 3.249 grams of the salt in 1 liter of water, and it is standardized against a known strength of thiosulfate as follows: Add 10 cc. of the acid iodate solution to 150 cc. of water containing 0.5 to 1 cc. of hydrochloric acid. Upon the addition of potassium iodide, iodine will be liberated according to the equation

$$HIO_3 + 5HI = + 3H_2O + 6I.$$

Starch is added and the titration is made to a colorless solution. From this titration the weight of copper to which 20 cc. of this solution are equivalent is accurately determined. A 20 cc. pipet is passed through a one-hole stopper and is allowed to remain in the acid iodate bottle. The end of the pipet is closed with a small rubber stopper. The exact copper equivalent of a thiosulfate solution is now easily found by titrating 20 cc. of the acid iodate solution whose copper equivalent is known with the thiosulfate as described above. The acid iodate remains constant indefinitly.

G. *Starch for Indicator.*—The best preparation for this purpose is a 0.5 per cent. solution of Kahlbaum's soluble starch. This is prepared as ordinary starch, but gives a perfectly clear solution which is very sensitive with iodine. If ordinary starch must be used it should be free from all cloudiness.

Detailed Description of the Method.

If the copper to be determined is present as metallic copper, 200–300 mg. are placed in a 300 cc. flask and dissolved in 5–10 cc. of 50 per cent nitric acid.

If the copper is present as cuprous oxide, it is filtered on a Gooch crucible through asbestos. The cuprous oxide is then dissolved through the Gooch crucible with 10–15 cc. of 30 per cent. nitric acid into a 300 cc. Erlenmeyer flask.

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If the copper is in the form of sulfide, it is filtered on a Gooch crucible which has a layer of asbestos one-eighth inch in thickness. The crucible is then placed in a small beaker of 50 cc. capacity, and 10 cc. of 50 per cent. nitric acid are added. The beaker is placed on a hot plate, and the nitric acid allowed to boil until all the black sulfide has gone into solution. The crucible is then washed off, and the solution transferred to a 300 cc. Erlenmeyer flask. The presence of the asbestos in the solution does not interfere with the titration of the copper.

If the copper to be determined is already in solution as sulfate, chloride, or other salt, sufficient solution is taken to give 100 to 300 mg. of copper.

Having obtained the copper in solution, preferably in a 300 cc. Erlenmeyer flask, the volume being between 50 and 60 cc., the acidity is adjusted to equal 4 to 5 cc. of concentrated nitric acid. A greater volume or acidity is to be avoided. The temperature should not be above 25°. Five cc. of the hypochlorite solution are now added to the copper solution, which is well mixed with a rotary motion. As soon as the color of the copper solution changes from a clear blue to a greenish tint, sufficient hypochlorite has been added. Another indication of a sufficient amount of hypochlorite is the liberation of chlorine. For weights of copper up to 200 mg., 2–3 cc. of the hypochlorite are sufficient. For larger amounts of copper more hypochlorite may be needed, but 5 cc. will be sufficient for any amount of copper which would be determined by this method. The reactions between the hypochlorous and nitrous acid require an appreciable time and the best results are obtained by allowing the solution to stand about 2 minutes before the addition of the phenol. This, however, is not essential. Ten cc. of the phenol solution are now added as quickly as possible, by blowing the solution from a pipet from which the tip has been removed.

The chlorine gas which remains in the flask above the liquid is removed by blowing into the flask and the sides are washed down with a jet of water. If the solution is allowed to stand at this point, nitrophenol will slowly form. Sodium hydroxide is therefore added until a very slight precipitate is obtained. The solution is now made acid with acetic acid; only a few drops should be required to dissolve the precipitate. Ten cc. of the potassium iodide are added and the titration made with the standardized thiosulfate. If great accuracy is required the titration is finished with a weak solution of thiosulfate.

The following are some results obtained by the method described above. The milligrams found and the error are calculated only to a point which is within the degree of accuracy of the apparatus used.

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DETERMINATION OF COPPER.

Copper taken. Mg.	Copper found. Mg.	Error. Mg.	Error. Per cent.
20.00	20.01	+0.01	+0.05
20.00	19.99	—0.01	—0.05
20.00	20.00	0.00	0.00
30.00	29.99	—0.01	—0.03
30.00	30.00	0.00	0.00
40.00	39.98	—0.02	—0.05
40.00	39.96	—0.04	—0.10
60.00	60.01	+0.01	+0.02
60.00	60.01	+0.01	+0.02
80.00	80.12	+0.12	+0.15
80.00	80.03	+0.03	+0.04
80.00	79.98	—0.02	—0.02
80.00	79.98	—0.02	—0.02
100.00	100.00	0.00	0.00
100.00	99.99	—0.01	—0.01
120.00	119.95	—0.05	—0.04
140.00	140.00	0.00	0.00
160.00	160.00	0.00	0.00
160.00	160.00	0.00	0.00
180.00	180.00	0.00	0.00
180.00	180.00	0.00	0.00
200.00	200.00	0.00	0.00
200.00	199.9	—0.1	—0.05
203.2	203.2	0.00	0.00
220.2	220.1	—0.1	—0.05
240.0	240.0	0.00	0.00
240.0	240.2	+0.2	+0.08
261.6	261.6	0.00	0.00
280.0	280.0	0.00	0.00
280.0	280.3	+0.3	+0.10
300.0	300.1	+0.1	+0.03
320.0	319.9	—0.1	—0.03
320.0	319.9	—0.1	—0.03
340.0	340.0	0.00	0.00

NOTE.—The sum of the + and — errors very nearly equals zero.

For the opportunity of carrying out this work I wish to thank Dr. N. B. Foster and for assistance with the analytical work Mr. A. W. Thomas.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UTAH EXPERIMENT STATION.]

THE OCCURRENCE OF POTASSIUM NITRATE IN WESTERN AMERICA.

BY ROBERT STEWART.

Received October 18, 1911.

About one year ago a sample of material was received at this laboratory for chemical analysis. The material was almost completely soluble in water and the analysis showed that it contained 12.79 per cent. of nitric

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nitrogen and 35.06 per cent. of potassium. The discoverer stated that it was found in large quantities in Southern Idaho, about 35 miles northeast of Soda Springs. This deposit was examined by the writer and others in June of this year. The nitrate was found in a cave occurring in red sandstone. The cave, which is located in a mountainous country at an elevation of 7,000 feet, is very small and contained probably 25 pounds of the nitrate. The sandstone roof of the cave contained crevices through which the nitrate had been carried by percolating water, the nitrate being deposited on the roof of the cave on the evaporation of the water. The position of the deposit and the nature of the surrounding country indicated that the nitrate could have been carried only through the sandstone by percolating water. The position of the deposit, high up in a mountainous country, far above any irrigating systems, precludes the possibility of its recent formation by bacterial action under the influence of irrigation water. Within a few miles of this deposit, there occur large deposits of sodium chloride which is at present being mined for domestic use.

Two samples of this material were collected for analysis. A sample of the sandstone, which appeared to have been stained with the nitrate, was broken off the face of the cliff about 100 yards above the cave. This was also analyzed. The results of the analysis are recorded in Table I.

TABLE I.—COMPOSITION OF CRUDE NITRATE AND SANDSTONE.

	No. 1. Nitrate.	No. 2. Nitrate.	No. 3. Sandstone.
Residue insoluble in water	4.22	2.73	98.21
Nitric nitrogen	11.12	11.48	0.127
Ammoniacal nitrogen	None	None	None
Calcium	2.91	2.12	..
Magnesium	0.11	0.17	..
Potassium	30.89	31.55	0.18
Sulfur	1.54	1.58	..
Chlorine	Trace	Trace	..

These results indicate that this material is crude potassium nitrate with some calcium sulfate. Deposits of nitrates have been reported elsewhere in Western America.[1] Samples have been received here from the southwestern part of this State near the Utah-Nevada line and from the central part of the State in Wayne County. A sample received from Pocatello, Idaho, contained 0.22 per cent. ammoniacal nitrogen, 2.59 per cent. nitric nitrogen, and 7.89 per cent. potassium.

Although the nitrate has not been found in quantities of commercial importance, the fact that it does occur in sandstone deposits is of interest just now for two reasons. It may indicate that water-soluble potassium occurs in quantities of commercial importance in the arid West. This

[1] Dunn, *Exp. Sta. Record*, 18, 430.

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is a question worthy of investigation by our national Geological Survey. It may have some bearing on the recent discovery[1] that nitrates are the predominating constituents in some of the western soils impregnated with alkali. The occurrence of these nitrates has been attributed to their formation by bacterial action at the present time. The existence of deposits of nitrates in the country rock in widely distributed areas in the arid West may have some connection with the occurrence of excessive quantities of nitrates in these agricultural soils.

LOGAN, UTAH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MINNESOTA.]

A CHEMICAL STUDY OF LIGNITE. PART II. THE VOLATIL CONSTITUENTS.[2]

BY G. B. FRANKFORTER AND ANDREW P. PETERSON.

Received March 8, 1911.

In the proximate analysis of lignite, the determination of the volatil constituents is unquestionably of great importance, and like the determination of moisture is deserving of special attention. A considerable portion of the volatil combustible matter in lignite, as determined in the proximate analysis of coal, seems to consist of small particles of carbon carried off by the liberated gases and by the moisture. This is evident from the fact that in addition to the flame produced by the burning of the gaseous constituents themselves, particles of solid combustible matter are carried upward by the gases and appear for an instant as glowing sparks before being completely oxidized. These solid particles are especially noticeable if the lignite contains a large amount of moisture or if the determination is made without first thoroughly drying the sample. Even though the crucible lid fits perfectly, these particles are thrown off when the heat is applied as indicated in the ordinary analysis of bituminous coal. The volatil constituentsmay be varied from 5 to 12 per cent. by slowly or rapidly raising the temperature to a red heat. The variation is more noticeable, however, in the undried lignite. It was found that not only the quantity of volatil matter but also the composition of the gas varied, depending upon the heating and whether or not the lignite contained its hygroscopic water.

The first experiments were made with the idea of determining the quantity of volatil matter, both by weight and by volume as compared with good bituminous coal. Accordingly, determinations were made by the ordinary method and by heating in an atmosphere of hydrogen.

The samples examined came from the extreme limits of the Dakota, the Canada and the Alaska coal belts. Samples from these different

[1] Bulletins Nos. 155 and 178, Colorado Agricultural Experiment Station.

[2] For the first paper see THIS JOURNAL, 29, 1488 (1907).

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localities were found to vary considerably in their physical properties, indicating that they must have been formed under different physical conditions. Those from the south are brown, slightly resembling good peat. They contain more moisture than those from farther north. They also seem to slack more readily. One of the characteristic features of the southern lignite is the tendency to break up into more or less laminated forms on losing moisture, while those from farther north, on losing moisture, break up with a slightly conchoidal fracture. The Saskatchewan, Alberta and Alaska lignites are darker than the lignite from the beds of southern North Dakota and slightly resemble ordinary anthracite in both color and fracture.

The regular proximate analyses were made according to the Report of the Committee on Coal Analyses.[1]

As already stated,[2] the lignites vary widely in the amount of moisture they contain. Some of the samples from the southern belt contain more than 40 per cent. of moisture or nearly twice as much as samples from the extreme north. This is due partly to the structure of the coal and partly to the fact that most of the beds in the south are very wet, while most of those in the north are comparatively dry.

In order to make the analyses as nearly comparable as possible, the samples were taken just as they came from the mines and dried in air until they had reached an equilibrium.

Under ordinary circumstances the lignites exposed to the air continued to lose moisture until they reached an equilibrium at from 10 to 12 per cent. At this point the loss of moisture practically stops if the lignite exists in pieces of moderate size. If the samples are pulverized, the moisture drops to 7 or 8 per cent. before an equilibrium is reached.

Samples 2 and 3 contain more than the average equilibrium amount of moisture, partly because they seem to be a little more compact, and partly because they were in larger pieces than the others. All of the samples were air-dried in the form in which they came from the mine.

The samples examined were as follows:

1. North Dakota.
2. Saskatchewan, Canada.
3. Alberta, Canada.
4. Klondike in Alaska.
5. Beaver Hill, Alaska.

For convenience, the above numbers have been used to represent the different samples.

The proximate analyses gave the following:

[1] THIS JOURNAL, 21, 1116–1145 (1899).

[2] *Ibid.*, 29, 1488.

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Sample.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Moisture	12.95	15.95	22.50	10.20	11.10
Volatil combustible matter.	36.45	34.40	28.30	36.65	37.20
Fixed carbon	42.77	44.38	45.40	48.40	46.43
Ash	4.83	5.27	3.91	4.75	5.27
Sulfur	0.90	0.82	0.70	..	..

Following the above determinations, ultimate analyses of the first three lignites were made. Calculating to moisture-free samples, the results were as follows:

Sample.	No. 1.	No. 2.	No. 3.
Carbon	62.90	66.42	68.10
Hydrogen	4.30	3.78	4.21
Nitrogen	0.81	1.09	1.12
Sulfur	1.03	0.98	0.90
Oxygen	25.46	21.43	20.67
Ash	5.50	6.30	5.00

Carbon and hydrogen were determined by the regular combustion, nitrogen by the Kjeldahl method and sulfur from the residue of a Parr calorimeter combustion. The ash was calculated from the proximate analysis.

Determinations in an Atmosphere of Hydrogen.—In order to compare the volatil matter obtained in the above proximate analyses, with result, obtained by heating at the same temperature in an atmosphere of hydrogen, a special apparatus was made, whereby the air could be entirely excluded during the process of heating. Various forms of apparatus were tried. The one which gave best results (see Fig. 1) consisted of a

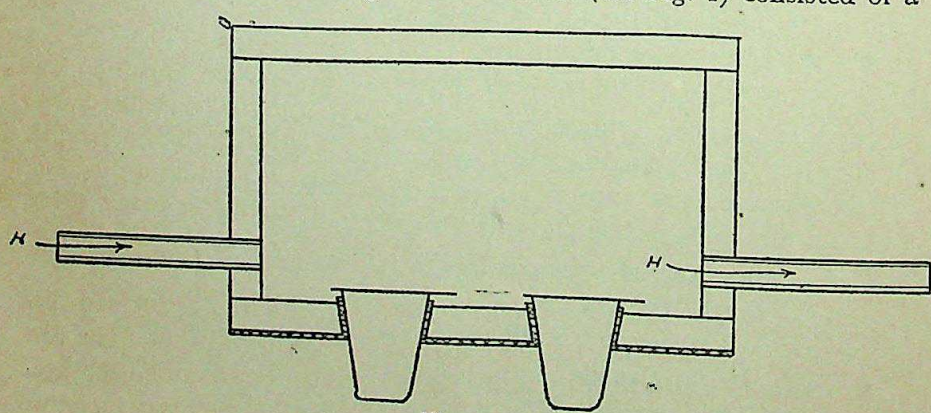

Fig. 1.

graphite muffle so arranged that the open end could be securely closed. Through the bottom of the muffle four holes were drilled of such size that platinum crucibles would fit in perfectly. By carefully fitting the crucibles with asbestos paper, they were made practically gas-tight. With this apparatus four analyses could be made at a time. Two small

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holes were bored through the side of the muffle in order that hydrogen could be passed through during the heating. Known weights of lignite were then placed in the crucibles, the air driven out by hydrogen and the determination made by heating in the regular manner at a red heat. In each case duplicate determinations were made.

The following table shows the difference between the amount of volatil matter as determined in an atmosphere of hydrogen and in air under the same conditions.

Sample.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Volatil matter in hydrogen..	28.51	28.60	28.79	28.65	28.57
Volatil matter in air.....	35.15	36.20	36.50	36.65	37.20

Destructive Distillation.—That the volumes of gas obtained by destructive distillation of the above samples of lignite might be compared, a series of determinations was made by heating a known quantity of lignite in a platinum distilling flask until all of the volatil material had passed off. The amount of gas was found to vary widely not only in samples of lignite obtained from different localities but also in those obtained from the same locality.

Samples from the far north, including Canada and Alaska, seemed to give more gas than those found further south in the Dakotas.

The following table represents the volumes of gas per gram obtained by heating in a platinum distilling flask at a bright red heat:

Sample.	No. 1.[1]	No. 1a.[1]	No. 2.	No. 4.
Volume of gas in cc. from dried lignite.....	400	376	420	450
Volume of gas in cc. from undried lignite.....	500	540	601	620

The total quantity of gas was found to vary widely, especially when the long narrow necked platinum distilling flask was used.

On carefully studying the gases, it was found that the variation was due to moisture in the coal, some of which was probably changed into hydrogen and carbon monoxide by the sudden heating of the sample. This was evident from the analysis of the gas. The platinum distilling flask was therefore discarded and a series of determinations made, using a special shaped iron retort so as to avoid the error resulting in the formation of water gas.

The pulverized lignite was placed in the air-tight iron retort and distilled at a temp. of 800–850° until the gas ceased to pass off. The distillates were led into cooled flasks for the purpose of condensing the water and tarry products. Two flasks were used for condensing the moisture and other readily condensable gases. The first one was kept at 25–30°; it condensed practically all of the water and most of the tar. The second was cooled by ice-water; it condensed in addition to a very small amount

[1] Samples 1 and 1*a* represent the southern and northern North Dakota lignite. No. 1*a* came from northern North Dakota and in appearance is a mean between the southern Dakota and Saskatchewan lignites.

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of water, a white waxy substance which melted at room temperature and which readily oxidized to a dark oily liquid. This white substance was found in all the lignites. It is under investigation at the present time.

The gases were then led into a gasometer but connections were made so that at any time during the distillation, samples of the gas could be drawn off for analysis before they entered the gasometer.

Destructive Distillation of North Dakota Lignite.—North Dakota lignite was subjected to destructive distillation in the apparatus above mentioned. The moisture and the tar were weighed and the gas measured. A number of analyses were made on the same sample.

Three determinations gave the following:

	No. 1.	No. 2.	No. 3.
Fixed carbon and ash	52.60	52.40	52.50
Water	27.20[1]	35.00[1]	36.30
Tar 1st bottle	0.70	0.70	0.70
Tar 2nd bottle	0.70	0.30	0.30
Gas at 0° and 760 mm. liters per 100 grams	17.00	12.50	15.50

An average sample from each distillation was then analyzed. Inasmuch as it was not found convenient to remove the air from the apparatus before beginning the experiments, corrections were necessary in order that the true composition of the gas might be determined. These corrections are found under the columns indicated as air-free gas.

Analysis of Gases.

The gases obtained from distillations 1 and 3 were analyzed with the following results:

	No. 1.		No. 3.	
	Found.	Calculated as air-free.	Found.	Air-free.
CO_2	36.0	41.0	34.5	38.1
Unsaturated hydrocarbons	0.5	0.6	2.0	2.3
O_2	3.1	1.0	3.6	1.6
CO	11.3	12.8	12.2	13.8
CH_4	..	..	24.5	27.5
H_2	..	..	12.5	13.0
N_2	..	..	10.7	3.7

The quantity of oxygen is unusual. After allowing for the oxygen of the air in the apparatus at the beginning of the process, an excess amounting to over 1 per cent. was found in the gas although no signs of leakage in the apparatus could be detected.

The quantity of unsaturated as well as of saturated hydrocarbons is extremely low in all of the lignites. This doubtless accounts for the fact that they are practically smokeless.

Analyses were then made of different samples of gas taken during successive stages of the distillation. The following results were obtained:

[1] Some of the water was lost by being sucked back into the retort after distillation.

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Sample taken.	After 500 cc.	After 3 liters.	After 7 liters.	After 8 liters.	After 10 liters.	At end of run.
CO_2	51.20	45.00	38.00	28.00	26.00	26.00
Unsaturated hydrocarbons	0.10	4.40	3.80	1.20	0.20	0.30
O_2	5.40	0.20	0.0	0.80	0.20	1.80
CO	5.60	13.60	12.00	15.00	14.40	12.00
CH_4	0.0	24.40	Not anal.	28.00	26.00	Not anal.
H_2	0.0	11.30	Not anal.	21.00	29.00	Not anal.
N_2	37.70	1.10	Not anal.	7.00	4.20	Not anal.

In the early stages of the distillation, carbon dioxide passed off more rapidly than the other gases, as will be seen from a glance at the above table. After about half of the gas had been driven off, the percentage remained practically constant. This, however, was not the case in the

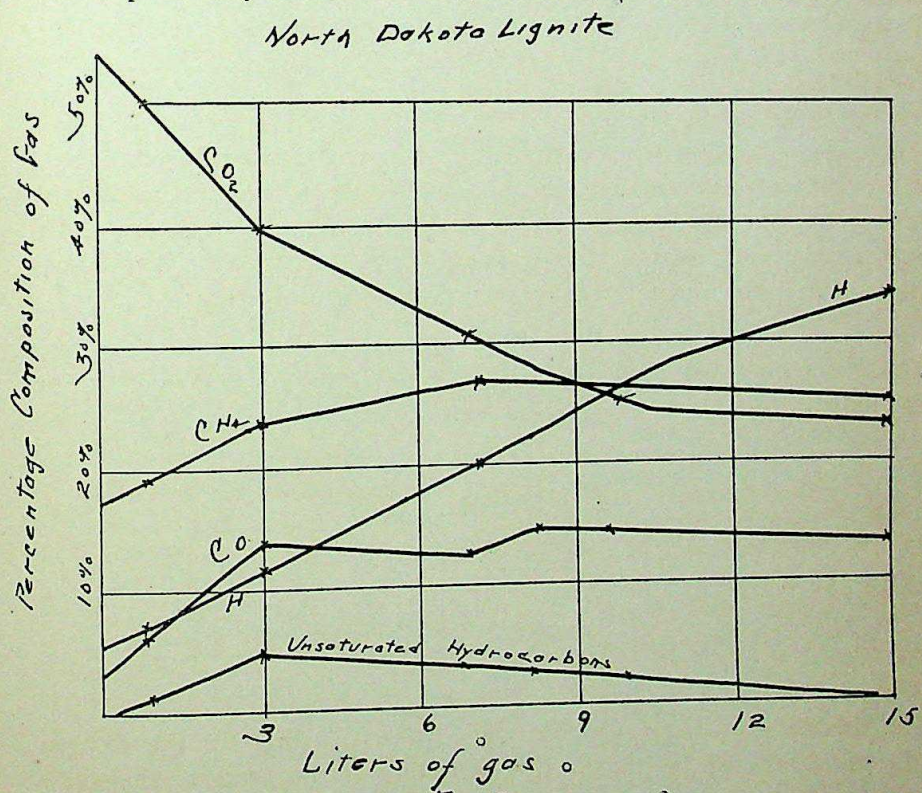

Fig. 2

other samples examined. The large amount of nitrogen in the first 500 cc. of gas is due to the fact that the air had not been removed from the apparatus.[1]

[1] In order, however, to avoid the error which would have occurred on account of air in the first 500 cc. of gas as indicated in the above tables, analyses were not used in plotting this and other curves until at least one liter of gas had been drawn off. The marks on the curves indicate the points at which samples were taken for analysis.

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The preceding diagram (Fig. 2) will give at a glance the composition of the gas at different stages of the distillation:

Destructive Distillation of Saskatchewan Lignite.

Three samples taken from the mines at Bienfait were subjected to the same process of distillation and at the same temperature as those of North Dakota with following results:

	No. 1.	No. 2.	No. 3.
Fixed carbon and ash	55.50	52.00	52.00
Water	28.00	..	28.00
Tar 1st bottle	0.34	..	0.40
Tar 2nd bottle	0.20	..	0.20
Gas liters per 100 grams	26.00	26.00	26.00

Analyses of average samples of the gas gave the following:

	No. 1.		No. 3.	
	Found.	Air-free.	Found.	Air-free.
CO_2	28.00	29.80	27.40	29.30
Unsaturated hydrocarbons	0.40	0.40	0.40	0.40
O_2	1.10	0.0	2.60	1.40
CO	12.40	13.00	15.10	16.30
CH_4	17.20	18.00	..	..
H_2	30.00	31.80	..	..
N_2	10.90	7.00	..	..

Analyses were then made of different samples of the gas taken during successive stages of the distillation. The following results were obtained:

Sample taken.	After 5 liters.	After 10 liters.	At end.
CO_2	55.60	26.00	16.20
Unsaturated hydrocarbons	1.20	1.00	0.0
O_2	0.80	0.0	0.40
CO	13.00	10.00	17.00
CH_4	17.20	20.60	14.10
H_2	12.20	41.30	41.80
N_2	0.0	1.10	10.50

This gas differed considerably from the North Dakota sample in the total amount of carbon dioxide and in the relative amounts of H and CH_4 evolved, as is graphically shown in the following diagram (Fig. 3).

Destructive Distillation of Alberta Lignite.

Three samples were taken from the mines at Edmonton and distilled exactly as in the previous samples, with the following results:

	No. 1.	No. 2.	No. 3.
Fixed carbon and ash	49.90	49.50	48.80
Water	32.10	33.90	32.10
Tar 1st flask	1.70	1.50	1.50
Tar 2nd flask	0.20	0.20	0.70
Gas liters in 100 grams	13.00	18.00	23.00

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Analyses of three average samples of the gas gave the following:

	No. 1.		No. 2.		No. 3.	
	Found.	Air-free.	Found.	Air-free.	Found.	Air-free.
CO_2	14.60	16.80	15.60	16.80	18.00	18.90
Unsaturated hydrocarbons.	0.80	0.90	0.10	0.20	0.80	0.90
O	6.00	4.50	2.30	0.40	0.90	0.0
CO	8.90	10.40	14.20	15.40	14.10	14.80
CH_4	21.50	24.50	20.30	22.00	24.80	26.10
H_2	31.30	36.00	32.40	37.70	33.50	35.20
N_2	16.90	7.90	15.10	7.50	7.90	4.10

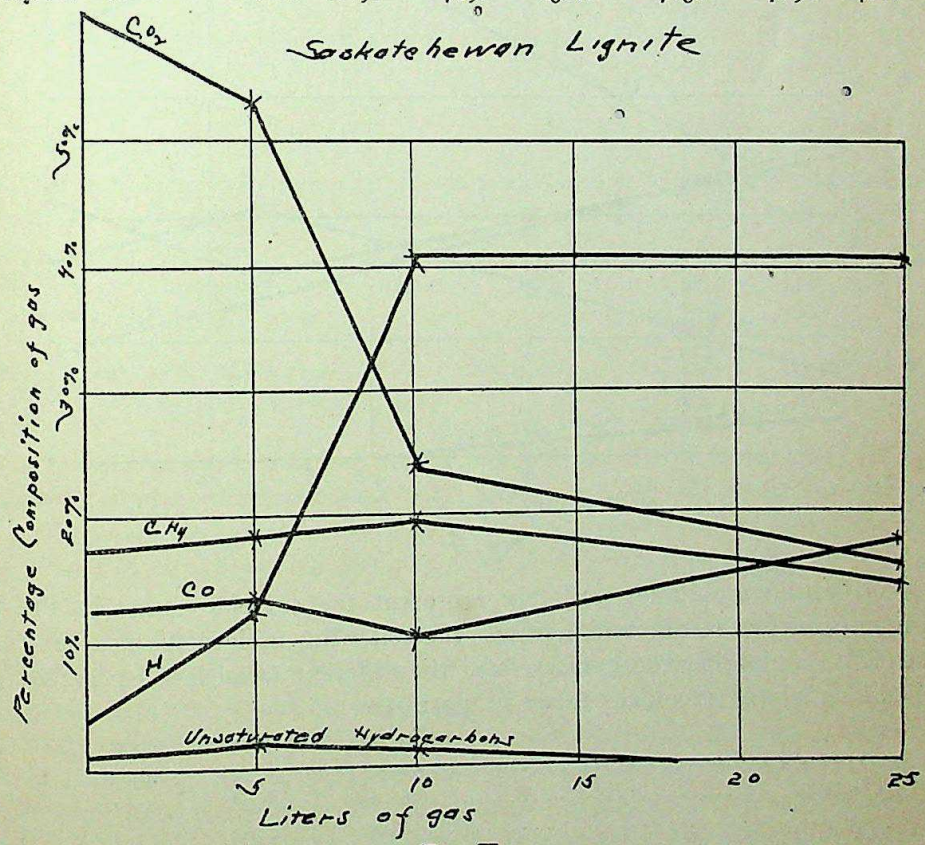

Fig. 3

Analyses were made of different samples of the gas taken during successive stages of the distillation, with the following results:

Sample.	After 3 liters.	After 15 liters.	Finish.
CO_2	21.60	14.80	20.80
Unsaturated hydrocarbons	2.70	0.00	0.00
O_2	1.90	0.00	0.00
CO	9.40	20.60	16.80
CH_4	22.20	15.70	19.40
H_2	24.10	42.60	35.70
N_2	8.10	6.30	17.30

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The following diagram (Fig. 4) will show well the way in which the proportion of gases changes during the distillation:

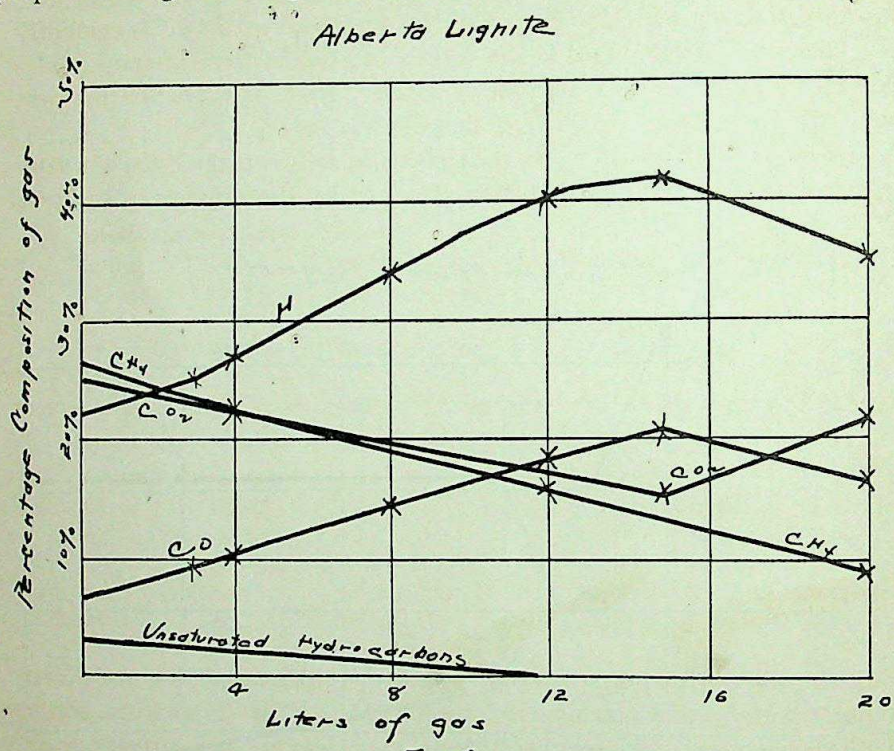

Fig. 4

As the above samples probably represent the extreme range in the composition of the different lignites, the following table will serve as a means of comparing the lignites from the different localities. Averages of three analyses have been taken in most cases.

	N. Dakota.	Saskatchewan.	Alberta.
Coke	52.50	53.20	49.40
Water	36.30	28.00	32.70
Tar	1.00	0.60	1.90
Gas liters in 100 grams	15.00	26.00	18.00

Comparison of Gases (Calculated as Air-free).

	N. Dakota.[2]	Saskatchewan.[1]	Alberta.
CO_2	38.10	29.80	17.50
Unsaturated hydrocarbons	2.30	0.40	0.70
O_2	1.60	0.00	1.60
CO	13.80	13.00	13.50
CH_4	27.50	18.00	24.20
H_2	13.00	31.80	36.30
N_2	3.70	7.00	6.50

[1] Average sample of distillation No. 1 of the Saskatchewan lignite.
[2] Average sample of distillation No. 3 of North Dakota lignite.

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Comparing the amounts of coke with fixed carbon and ash of the proximate analysis, it will be seen that there is considerable difference; due, doubtless, to incomplete distillation as the temperature of 830° is evidently not sufficient to drive off all of the volatil matter in some of the samples (see Porter and Ovitz, Bureau of Mines, *Bull.* I). Distillation was apparently complete, however, in the Alberta lignite.

The following table will show the difference between the coke left after the distillation and the fixed carbon obtained by the proximate analysis:

	N. Dakota.	Saskatchewan.	Alberta.
Distillation, coke including ash.....	52.50	53.20	49.40
Fixed carbon, including ash.....	47.60	49.65	49.30
	4.90	3.55	0.10

The following table shows the relative amounts of hygroscopic water as compared with the total amount found by destructive distillation:

	N. Dakota.	Saskatchewan.	Alberta.
Per cent. of water obtained by distillation.....	36.30	28.00	32.70
Per cent. of hygroscopic water.....	12.95	15.96	22.50
Water produced by distillation.....	23.35	12.04	10.20
Per cent. of H present (by ultimate anal.).....	4.30	3.77	4.21

Calculating the amounts of water found to the dry analysis, the North Dakota lignite would consume 2.98 per cent. of the H to form water, the Saskatchewan 1.59 and the Alberta 1.47, leaving respectively, 1.32, 2.18 and 2.80 per cent. of H to be evolved either as free hydrogen or in the form of hydrocarbons.

From the above data and from the moisture determinations in samples from different localities[1] it is apparent that the composition of the various lignites depends somewhat upon the locality. The southern samples contain more moisture than those from farther north. The total amount of volatil constituents, however, increases slightly as we go northward. The individual gases seem to vary but not regularly. Carbon monoxide is practically constant and marsh gas changes but little. There is, however, an increase in the amount of hydrogen as we pass northward. On the whole, there is but little difference in the volatil constituents from the different samples, although there is a distinct difference in the general physical appearance.

MINNEAPOLIS, MINN.

NOTES.

Preparation of Stannic Iodide and Its Solubility in Certain Organic Solvents.—In the preparation of stannic iodide for use in this laboratory

[1] Part I, THIS JOURNAL, 29, 1488.

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recently, recourse was had to the method of Schneider,[1] depending on the reaction of tin and iodine in a medium of carbon disulfide. It was thought desirable to avoid, if possible, the use of the latter volatil and unpleasant reagent, and accordingly, after a little experimentation, an attempt was made to substitute carbon tetrachloride therefor. It has been found that the tetrachloride forms an excellent substitute for the disulfide in this process, and that it offers some further advantage in the matter of the purification of the product by crystallization from solution. The following is the method finally adopted: In a long-necked Kjeldahl flask there were placed twelve to fifteen grams of tin and forty grams of iodine, and these were covered with about 75 cc. of carbon tetrachloride. The neck of the flask was fitted with a cork stopper bearing a small reflux condenser. The bottom of the flask was then heated gently with a burner until the tetrachloride commenced to boil, when the flame was lowered until just sufficient to maintain the ebullition. The reaction between the tin and the iodine usually begins before the boiling point of the medium is reached, and continues of itself, supplying considerable heat. As the concentration of the iodine becomes less, the end point may be hastened by heating the solution more strongly. The end of the reaction is indicated by the complete change of the violet color of the solution to deep orange, and the absence of violet fumes of iodine above the liquid. A slight excess of tin is desirable to avoid the necessity of removing an excess of iodine by distillation after the reaction is over.

The stannic iodide is much more soluble in the boiling carbon tetrachloride than at ordinary temperatures. Accordingly, the boiling solution is decanted through a folded filter, preferably in a steam-jacketed funnel, the filter washed with boiling tetrachloride, and the filtrate cooled in ice-water. An abundant precipitation of small crystals of stannic iodide takes place; the mother liquor may be drained by centrifugation or otherwise, and evaporated for the production of a second small crop of crystals. The crystals may be further purified for use by again dissolving in hot tetrachloride and recrystallizing, or by sublimation as used by Fitzgerald.[2]

Two determinations of the solubility of stannic iodide in carbon tetrachloride gave the following figures:

Temp.	Sp. gr. of solution.	Grams of SnI_4 in 100 cc. solution.	Grams of SnI_4 in 100 grams solution.
22.4	1.59	8.35	5.25
50.0	1.63	20.47	12.50

It has also been found that chloroform may be used in place of the tetrachloride, but its lower boiling point offers one objection to its use.

[1] *Pogg. Ann.*, 127, 624 (1886).

[2] THIS JOURNAL, 29, 1694 (2907).

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The range of solubility of stannic iodide in chloroform is of the same order as in carbon tetrachloride, and the iodide may be crystallized from it in the same manner.

The following figures were obtained for the solubility of stannic iodide in chloroform and in benzene:

Solvent.	Temp. °C.	Sp. gr. of solution.	Grams of SnI_4 in 100 cc. solution.	Grams of SnI_4 in 100 grams solution.
$CHCl_3$	28.0	1.50	12.32	8.21
C_6H_6	20.2	0.95	12.02	12.65

Stannic iodide appears to be fairly stable in contact with the air during ordinary manipulations, and while in solution in carbon tetrachloride, chloroform, etc. Under the prolonged action of moist air, however, it forms the oxide.

An analogous procedure may be used for the preparation of the corresponding bromide. The heat evolved in the reaction with bromine is considerably more than with iodine, and it is advizable to place the tin alone in the flask, covered with a layer of tetrachloride, and to add the bromine subsequently, dissolved in a further amount of tetrachloride, in small portions at a time, through the open end of the condenser. The reaction takes place spontaneously, without the addition of external heat; the reaction flask may be kept in a bath of cold water with advantage. The bromide is much more sensitive to the action of moist air than the iodide, and on this account much more care is necessary in handling the product to assure exclusion of water vapor.

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WASHINGTON, D. C.

Lecture Table Experiment on Nascent Hydrogen.—Many experiments have been proposed to convince students that hydrogen in the process of formation upon the surface of a metal is especially active. The general principle of the following experiment has of course no claim to originality, but it has been found that the particular reagents suggested make the demonstration especially rapid and striking.

A large Erlenmeyer flask is partly filled with sulfuric acid, 15 cc. of the concentrated acid to the liter. A few grams of magnesium ribbon are first introduced, and then enough of a dilute solution of ferric chloride and potassium ferricyanide to impart to the mixture a decided color. After agitating the flask for a short time, it is seen to be filled with a finely divided deep blue precipitate. Next it is proved in the usual manner that the several reagents separately do not produce a similar effect: (*a*) magnesium is introduced into a dilute (neutral) solution of ferric chloride and potassium ferricyanide; (*b*) dilute sulfuric acid and magnesium sulfate are added to a second portion; (*c*) hydrogen is bubbled through a third portion.

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The concentration of the acid should not vary too widely from that suggested. If the acid is much more dilute, the action is too slow; if much more concentrated, the reaction products are pale green rather than deep blue.

The point at issue can easily be understood by a class without any statement of the composition of the brown solution or that of the blue reaction products.

G. S. FORBES.

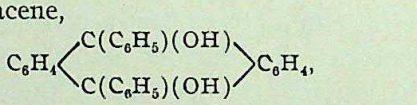
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE ACTION OF ETHYL MAGNESIUM BROMIDE ON ANTHRAQUINONE.[1]

BY LATHAM CLARKE AND PAUL WHITTIER CARLETON.

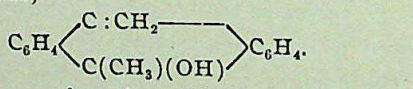
Received August 30, 1911.

It has been shown by Haller and Guyot[2] that an excess of phenyl magnesium bromide reacts with anthraquinone forming 9,10-diphenyl-9,10-dihydroxydihydroanthracene,



while an excess of the quinone gives phenyloxanthrone (or phenyloxanthranol).

Guyot and Staehling[3] prepared analogous compounds from methyl anthraquinone, using phenyl and naphthyl magnesium bromides. They also treated anthraquinone with methyl magnesium bromide, which produced 9,10-dimethyl-9,10-dihydroxydihydroanthracene, and this compound readily lost one molecule of water, giving 9-methene-10-methyl-hydroxydihydroanthracene,



The action of ethyl magnesium bromide on anthraquinone was studied in this laboratory in 1907 by Clarke and Victor Cobb, who found that the normal action was to give 9,10-diethyl-9,10-dihydroxydihydroanthracene, but certain other compounds were formed by side reactions. These last we were prevented from studying, on account of the departure of Mr. Cobb from Cambridge.

In the autumn of 1910 this study was taken up by the present writers. We have found that with an excess or ethyl magnesium bromide, the anthraquinone is converted into the di-ol; and when an excess of the quinone is used, the product is ethyloxanthranol. The di-ol is very sus-

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Paul Whittier Carleton.

[2] *Compt. rend.*, 138, 327, 1251 (1904); *Bull. soc. chim.*, 31, 795, 979 (1904).

[3] *Bull. soc. chim.*, 33, 375 1104 (1905).

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ceptible to the action of dehydrating agents, and the side products obtained in the experiments of Clarke and Cobb and later by us, are dehydration products, formed from the di-ol by the excess of acid used to acidify the reaction mixture after the usual decomposition of the organomagnesium compound with water.

The di-ol is a white crystallin compound, which melts at 172°. The crystals obtained from ether or alcohol solutions contain ether or alcohol of crystallization, but in either case so loosely held that on standing in the air the crystals quickly effloresce to a white powder. Both hydrogen atoms of the di-ol could be replaced by alkyl groups, and the dimethyl and diethyl ethers were prepared. All attempts to substitute the hydroxyl groups by halogens failed.

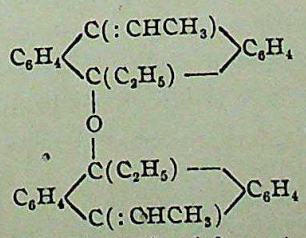
Dilute hydrochloric or sulfuric acid acted on the di-ol, quickly turning it to a yellow color, and giving a mixture of two new substances, which could be separated only by a laborious process of fractional crystallization. These new substances were lemon-yellow in color, one crystallized in rhombic plates and melted at 161°, the other crystallized in prisms and melted at 226°. The longer the standing with dilute acid, the greater was the proportion of the higher melting compound, from which it seemed that the higher melting was formed from the lower melting.

Both these compounds had the same composition as shown by analysis:

Compound melting at 161°, Found: C, 89.27; H, 7.25.
Compound melting at 226°, Found: I, C, 89.48; H, 7.28.
Compound melting at 226°, Found: II, C, 89.53; H, 6.84.

Determinations of the molecular weights indicated that the molecule of each of these compounds contained two anthracene nuclei; the molecular weight found for the compound melting at 161° was 480; that for the compound melting at 226°, 425. These figures for the analysis and molecular weights point to the formula for each, $C_{36}H_{34}O$. The solubilities of both compounds were quite similar, but in the properties of the solutions there was one striking difference; the lower melting dissolved in alcohol, benzene, and such solvents, giving yellowish solutions, but the solutions of the higher melting were fluorescent.

We can now construct a very probable formula for the compound melting at 161°:



As will be seen, this formula is derived from two molecules of the di-ol,

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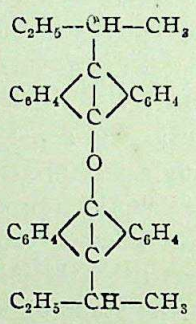
by the elimination of three molecules of water. By the splitting off of one water molecule, the two dihydroanthracene nuclei are joined together, while the splitting off of the other two gives the unsaturated ethylidene groups, which are analogous to the methene groups of Guyot and Staehling. This compound remains a derivative of dihydroanthracene, and *derivatives of dihydroanthracene do not exhibit fluorescence when in solution.*

We may now construct a possible formula for the compound melting at 226°:



This formula is obtained from that for the compound melting at 161°, by a migration of the two ethyl groups from the two different 10-positions in the dihydroanthracene nuclei, to the number 2-position in the ethylidene side chains which thereby become secondary butyl groups, the condition of unsaturation being broken. This migration taking place slowly accounts for the gradual change of the compound melting at 161° into its isomer, and since this new compound is a derivative, not of dehydroanthracene, but of anthracene, the fluorescence of the new compound is explained. A wandering of ethyl groups, similar to the case described above, and likewise brought about through the influence of dilute acids, has been shown by Zincke,[1] while the migrations of other groups in an analogous manner have been described by Bamberger[2] and Auwers.[3]

Experimental Part.

The ethyl magnesium bromide used in this research was prepared in the usual way, in ether solution. Since anthraquinone is but slightly soluble in ether, it was used in suspension and to the ethyl magnesium bromide derived from 90 grams of ethyl bromide, 30 grams of anthraquinone were added, together with about 50 grams of ether. The mixture was heated gently for four hours, then treated with sufficient ice-water to decompose the organomagnesium compounds, and acidified with dilute hydrochloric acid. As much anthraquinone remained visibly

[1] Zincke, *Ber.*, 34, 253 (1901).

[2] Bamberger, *Ibid.*, 38, 3607 (1910).

[3] Auwers, *Ber.*, 36, 1861 (1903); 38, 1697 (1905); 39, 3748 (1906); 43, 3094 (1910); 44, 588 (1911).

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unchanged, it was necessary to remove it by filtration, so the ether layer was drawn off and filtered. By setting the clear ether aside and allowing it to evaporate slowly, the di-ol was obtained in the form of rather large white crystals, but as the evaporation proceeded, anthraquinone crystals began to appear, and a reddish colored oil gathered on the sides of the crystallizing dish. It was found, subsequently, that if the acidification of the reaction mixture was so carefully carried out as to avoid an excess of free acid, this reddish oil was practically lacking, while the use of a large excess of hydrochloric acid gave much reddish oil and little or no di-ol. It was also found that by agitating vigorously the mixture of ethyl magnesium bromide and anthraquinone, the yield of the di-ol was much increased, so a mechanical stirring device was used in the later experiments. Without the stirrer, the yield of di-ol was from five to ten per cent. of the theoretical, calculated from the anthraquinone, while with the stirrer the yield was in one case as high as thirty-six per cent. of the theoretical.

The above-mentioned reddish oil was treated with alcohol with which a few drops of benzene had been mixed, and after a series of crystallizations, yielded two light yellow-colored compounds, one melting at 161° and the other at 226°, also some unchanged anthraquinone and a residue of a red tar, from which nothing definit could be isolated. The two yellow-colored compounds were later found to be identical with the substance formed from the di-ol by the action of dilute acids, an account of which is given later in this paper. The red tar was subjected to a distillation *in vacuo* and the distillate, which consisted only of a small fraction of the weight of the substance taken, was found to be diethyl anthracene, and was evidently some decomposition product of the red tar.

9,10-Diethyl-9,10-dihydroxydihydroanthracene.—The di-ol obtained as already described was crystallized from ether or benzene. A sample was dried *in vacuo* for analysis.[1]

Calculated for $C_{18}H_{20}O_2$:		C, 80.55; H, 7.50.
Found:	I.	C, 80.39; H, 7.08.
	II.	C, 80.71; H, 5.83.

A determination of the molecular weight was made in benzene by the freezing-point method.

0.0758 gram substance in 17.67 grams benzene gave Δ 0.080°.

0.1583 gram substance in 17.67 grams benzene gave Δ 0.130°.

In this last case the substance was not entirely dissolved.

Molecular weight:

Calculated for $C_{18}H_{20}O_2$:		268.
Found:	I,	268; II, 344.

[1] One of us had previously shown that this substance, when crystallized from ether, retains one molecule of ether of crystallization (*Ber.*, 41, 936). This compound also crystallizes with other solvents, as, for example, alcohol.

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Although in the second case the substance was not entirely dissolved, the simpler molecule was indicated and the one trustworthy value was confirmed. Since the solubility in benzene was exceeded, it is possible to calculate the solubility in benzene at its freezing point. We find that the 0.1583 gram should have caused a depression of 0.167°.

Evidently, then, 0.130/0.167 multiplied by 0.1583 is the approximate solubility in 17.67 grams of benzene. This gives one part of the di-ol as soluble in 140 parts of benzene.

Properties.—The di-ol crystallizes in white hexagonal prisms, cut off obliquely, which melt at 172°. The substance crystallizes well from other solvents; from acetone especially, beautifully formed crystals can be obtained. Soluble in alcohol, ether, acetone, chloroform, carbon tetrachloride and carbon disulfide; slightly soluble in cold benzene, but soluble in warm benzene; in naphtha it is not very soluble; glacial acetic acid dissolves it, especially if warmed, but soon acts upon it in a dehydrating manner. It is not soluble in sodium hydroxide. In acetic acid it is an oxidizing agent, acting upon potassium iodide to set iodine free. On standing exposed to the air of the laboratory, the white color changes to a dull yellow, and the melting point falls. It dissolves in concentrated sulfuric acid with an intense red color. If boiled in higher boiling neutral solvents, as xylene, the solution turned yellow, and on evaporation gave a yellow oil which could not be crystallized. Dehydrating agents had the same effect when attempts were made to split out two molecules of water. The benzene solutions in various experiments, zinc chloride, phosphorus pentoxide, calcium chloride, concentrated sulfuric acid, and hydrochloric acid gas were added, but in all cases uncrystallizable yellow oils were obtained. The di-ol was also fused with potassium acid sulfate in order to completely dehydrate it, if possible, but here also the resulting product was an oil.

Just as all attempts to completely dehydrate the diethyldihydroxydihydroanthracene failed, so all attempts to replace the two hydroxyls by halogen failed. Hydrochloric and hydrobromic acid gases were tried in benzene solution both with and without anhydrous sodium phosphate to take up the water. Phosphorus trichloride, oxychloride and pentachloride reacted violently with the substance giving off hydrochloric acid and leaving an oil. The yellow oil resulting from the action of phosphorus pentachloride was dissolved in low-boiling naphtha and this evaporated by a blast of air, when it left some rhombic plates, but any attempt to recrystallize these converted them into an oil.

The action of acetyl chloride, benzoyl chloride and acetic anhydride resulted similarly in most cases, that is, neither an acetate nor benzoate could be isolated, but instead there was produced a yellowish oil. The action of acetyl chloride on the dimethyl ether of the di-ol was tried,

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which procedure was suggested by the fact that the acetate of triphenylcarbinol can be made only in this way, but this was not successful. When the action of acetyl chloride on the di-ol was tried at room temperature, there resulted a cream-colored substance which caused blue fluorescence in methyl alcohol, and crystallized from it in clusters of needles, melting at 135.5–136°. These were dried *in vacuo* to constant weight and analyzed.

Found: C, 85.30, 85.36; H, 7.50, 7.75.

These analyses correspond to a formula $C_{16}H_{17}O$, but what such a formula could represent is not known.

By the action of zinc dust and glacial acetic acid, the di-ol was converted into diethylanthracene.

Dimethyl Ether of Diethyldihydroxydihydroanthracene.—This was made by adding to a hot concentrated solution of the dihydroxy compound in methyl alcohol a few drops of methyl alcohol in which hydrochloric acid gas had been dissolved. At once, the crystals of the dimethyl ether separated and were recrystallized from methyl alcohol, which acquired a slight blue fluorescence on the first crystallization, but on subsequent recrystallizations the fresh solvent remained colorless. The dimethyl ether is much less soluble than the dihydroxy compound, melts at 178°, and dissolves in concentrated sulfuric acid with a red color. It was dried to constant weight *in vacuo* over sulfuric acid and analyzed.

Calculated for $C_{18}H_{18}O_2(CH_3)_3$: C, 81.03; H, 8.14.
Found: C, 80.68; H, 8.25.

The diethyl ether was made by the same method. It is more soluble in ethyl alcohol than the methyl ether is in methyl alcohol.

Calculated for $C_{18}H_{18}O_2(C_2H_5)_2$: C, 81.43; H, 8.70.
Found: C, 80.90; H, 8.26.

Action of Dilute Hydrochloric Acid on the Di-ol.—When the di-ol was heated on the steam bath with water alone for several hours no change took place, but if the water were acidified with hydrochloric acid, the di-ol changed in color to yellowish orange. A solution containing but one per cent. of acid brought this about. With twice-normal hydrochloric acid, the di-ol turned yellow as soon as the suspension became warm on the steam bath, while several minutes were required when acid of a strength of one per cent. was used. On heating for some minutes with twice normal acid, the di-ol was completely transformed into a red oil, which, on cooling, solidified. This was warmed with ethyl alcohol, whereby an extract was obtained, and a yellow mass remained behind. The last was very slightly soluble in most solvents with the exception of benzene, but could not well be crystallized from benzene, however, as it separated as an oil. Alcohol was not at all a convenient solvent, since it dissolved so little substance, and it was ultimately found best as a process of crys-

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tallization to first use alcohol with a little benzene, then, on the next recrystallization, to use a mixture of two parts of alcohol and one of benzene. This yellow mass was soon found to be a mixture of two substances, one crystallizing in rhombic plates or octahedra, the other in prisms. The separation of these two was tedious since the solubilities were similar; but by continued fractional crystallization from the benzene and alcohol mixture it was possible to obtain small amounts of each in a pure condition. The rhombic form melted at 161°, the other at 226°. They were both lemon-yellow in color; both decolorized a chloroform solution of bromine as well as bromine water; both were oxidized by potassium dichromate to anthraquinone.

A more convenient way of preparing this mixture was not to heat at all, but to allow the di-ol to stand in dilute acid at room temperature using either hydrochloric or sulfuric acids, although hydrochloric was to be preferred. In the course of a few hours the color was changed perceptibly, but the mixture was allowed to stand four days, when the yellow mixture was filtered and washed free from acid. The wash waters had a slight blue fluorescence. The mass was then extracted with hot alcohol from which unchanged substance crystallized on cooling, while the substance which remained was largely that yellow compound which had the rhombic form, melting at 161°, but which required several crystallizations to purify it entirely. If the acid mixture were allowed to stand two weeks, a much larger proportion of the compound melting at 226° was found to be present. A mixture was nearly always obtained, but the longer the reaction mixture remained standing, the more of the higher melting form was produced.

The yellow compound melting at 161° was dried *in vacuo* and analyzed.

Calculated for $C_{36}H_{34}O$:	C, 89.57; H, 7.10.
Found:	C, 89.27; H, 7.25.

A molecular weight determination by the freezing-point method was made, although only a small sample of pure material was available.

Molecular weight:

Calculated for $C_{36}H_{34}O$:	484.
Found:	480.

Properties.—Yellow rhombic plates, melting at 161°. This compound is soluble to a slight extent in methyl alcohol, ethyl alcohol, acetone, ether, and glacial acetic acid. The solubility in the hot solvents is only slightly greater. Soluble in benzene and toluene.

The yellow substance melting at 226° was dried and analyzed.

Calculated for $C_{36}H_{34}O$:	C, 89.57; H, 7.10.
Found:	C, 89.53, 89.48; H, 7.27; 6.84.

The only sample at hand sufficiently pure for a molecular weight determination was small and was somewhat impure, due to a slight admix-

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ture of the lower melting substance. The freezing-point method was used.

Molecular weight:

Calculated for $C_{36}H_{34}O$:	484.
Found:	425.

Properties.—Yellow prisms, melting at 226°. Soluble in benzene and toluene; slightly soluble in methyl alcohol, ethyl alcohol, ether, acetone, and glacial acetic acid. The solutions show fluorescence.

Part of the expenses of this research were defrayed by a grant from the C. M. Warren Fund for Research, for which we wish to express our gratitude.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

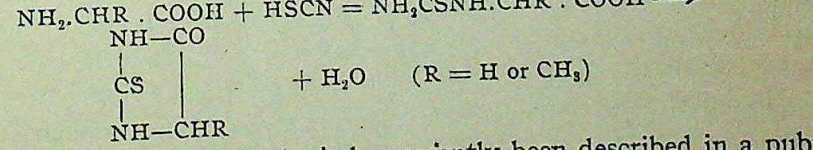
HYDANTOINS: THE SYNTHESIS OF 2-THIOHYDANTOIN.

[SEVENTH PAPER.]

BY TREAT B. JOHNSON AND BEN H. NICOLET.

Received November 13, 1911.

Two methods of synthesizing 2-thiohydantoin have recently been described in the literature. Komatsu[1] has prepared this compound by the action of potassium thiocyanate on glycocoll. He states that this amino acid reacts with the thiocyanate, in the presence of acetic anhydride, giving the hitherto unknown thiohydantoic acid, $NH_2CSNHCH_2$-COOH, which can be converted into the hydantoin by the action of strong hydrochloric acid. He also examined the behavior of potassium thiocyanate towards alanine and obtained 2-thio-4-methylhydantoin. The general reactions involved in these condensations are represented by him as follows:



$$NH_2.CHR.COOH + HSCN = NH_2CSNH.CHR.COOH \longrightarrow$$

$$\begin{array}{l} NH-CO \\ | \qquad | \\ CS \qquad | \\ | \qquad | \\ NH-CHR \end{array} + H_2O \qquad (R = H \text{ or } CH_3)$$

The second method of synthesis has recently been described in a publication from this laboratory.[2] We showed, for example, that ethyl acetyl- and benzoyldithiocarbamates, I, react smoothly with glycocoll or its ethyl ester, giving the corresponding acyl derivatives of thiohydantoic acid, II, with evolution of ethyl mercaptan. When these acyl derivatives, II, were digested with hydrochloric acid they were converted smoothly into 2-thiohydantoin, III. We also prepared 2-thio-4-methylhydantoin from alanine. The various transformations are represented as follows:

[1] *Memoirs Coll. Sci. and Eng.*, Kyoto Univ. (Japan), 3, 1 (1911).

[2] Wheeler, Nicolet and Johnson, *Am. Chem. J.*, 46, 456 (1911).

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$$\underset{(CH_3CO)\ \ I.}{C_6H_5CONHCSSC_2H_5} + NH_2CH_2COOH(C_2H_5) = \underset{(CH_3CO)\ \ II.}{C_6H_5CONHCSNHCH_2COOH(C_2H_5)}$$

$$\longrightarrow \underset{III.}{\begin{array}{l} NH-CO \\ | \quad\ \ | \\ CS \quad\ \ | \\ | \quad\ \ | \\ NH-CH_2 \end{array}} + C_6H_5COOH \text{ or } CH_3COOH$$

Since it was necessary to prepare large amounts of 2-thiohydantoin for certain investigations in progress in this laboratory, we naturally decided to employ Komatsu's method for the preparation of this compound. We find that 2-thiohydantoin can be prepared easily in this manner, but on the other hand, have made the very interesting observation that Komatsu's interpretation of the mechanism of the reactions is entirely incorrect. In this paper we shall describe a new method for preparing easily this 2-thiohydantoin, III, and also give a correct explanation of the behavior of potassium thiocyanate towards glycocoll in the presence of acetic anhydride.

Radenhausen[1] has shown that glycocoll and acetic anhydride react smoothly below 100°, giving acetylglycocoll,

$$NH_2.CH_2COOH + (CH_3CO)_2O = CH_3CONHCH_2COOH + CH_3COOH.$$

Komatsu has practically duplicated the conditions of Radenhausen's experiment in his directions for preparing thiohydantoic acid, and consequently it did not seem probable to the writer that the presence of potassium thiocyanate should prevent here the primary formation of this acetyl derivative. Furthermore, Curtius[2] has shown that acetylglycocoll possesses weak basic properties and combines with hydrochloric and sulfuric acids, giving the corresponding salts. These salts, however, are unstable, as might be expected, and readily undergo hydrolysis with water giving the original acid. If, now, acetylglycocoll was formed under the conditions employed by Komatsu, it might be expected that it would combine with thiocyanic acid, in the anhydrous solvent, forming a thiocyanate, V, which would then undergo a normal rearrangement, giving acetylthiohydantoic acid, VI. This could then undergo an inner condensation on further warming with anhydride and be converted into acetylthiohydantoin, VII, or 2-thiohydantoin, III, with loss of the acetyl radical.

The experimental data, which we have obtained, prove that these assumptions are correct. We find that glycocoll reacts with potassium thiocyanate, in the presence of acetic anhydride, giving an excellent yield of 3-acetyl-2-thiohydantoin, VII. We obtained no evidence of the formation of the thiohydantoic acid described by Komatsu. In fact it seems very probable that this investigator actually described an impure substance. The results of his sulfur determinations would indicate

[1] *J. prakt. Chem.*, 52, 438.

[2] *Ber.*, 17, 1662 (1884).

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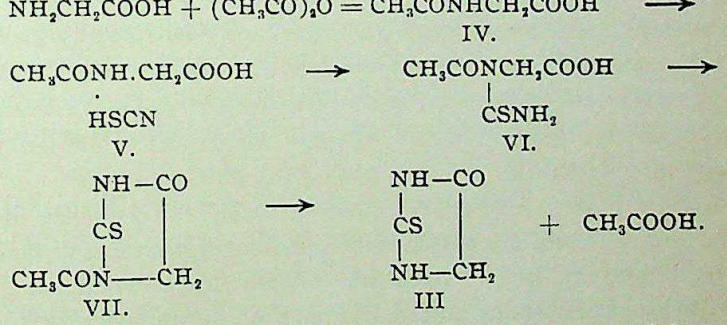
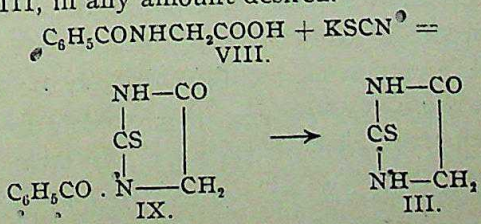
such a possibility. When the acetylthiohydantoin, VII, was dissolved in concentrated hydrochloric acid and the solution evaporated to dryness, pure 2-thiohydantoin, III, was obtained.

Furthermore, that aceturic acid is the primary product of the reaction in this synthesis is proven by the following facts: 2-Thiohydantoin and acetic anhydride do not react at 100° giving an acetyl derivative. Secondly, acetylglycocoll reacts with potassium thiocyanate under the conditions employed by Komatsu, forming almost a quantitative yield of the same 3-acetyl-2-thiohydantoin, VII, as was obtained from glycocoll. Therefore the acetic anhydride cannot be considered as a *catalytic agent*, as stated by Komatsu, and actually takes part in the reactions involved giving primarily aceturic acid, a fact which was entirely overlooked by Komatsu. The general reactions involved in the synthesis of 2-thiohydantoin from glycocoll, acetic anhydride and potassium thiocyanate, are therefore to be represented as follows:



The smooth formation of acetylthiohydantoin from acetylglycocoll by the action of potassium thiocyanate suggested that other acyl derivatives of this amino acid would likewise react with this reagent to form acylthiohydantoins. We therefore applied the reaction with hippuric acid, VIII. We now find that this acid reacts as readily as acetylglycocoll with potassium thiocyanate in acetic anhydride solution, forming 3-benzoyl-2-thiohydantoin, IX. This was then converted into 2-thiohydantoin, III, by hydrolysis with hydrochloric acid. Therefore, starting with hippuric acid, we have at hand a practical method of preparing 2-thiohydantoin, III, in any amount desired.



The investigation of the action of potassium thiocyanate on amino acids and their acyl derivatives is now in progress in this laboratory.

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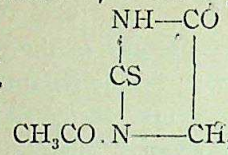
Experimental Part.

The Action of Potassium Thiocyanate on Glycocoll. 3-Acetyl-2-thiohydantoin,



.—Two grams of pure glycocoll and 2.6 grams of potassium thiocyanate were thoroughly ground together in a mortar and suspended in 10 cc. of acetic anhydride (Kahlbaum's). This mixture was then gently heated on a steam bath when there was an immediate reaction, with evolution of heat, and within three minutes a clear orange-colored solution was obtained. In order to duplicate as closely as possible the conditions of Komatsu's[1] experiment, the solution was then heated for 30 minutes to thoroughly complete the reaction. The thick viscous liquid was then cooled and poured into about 5–6 times its volume of cold water, when this acetyl hydantoin separated in crystalline condition. The yield was 3.5 grams, corresponding to 83.3 per cent. of the theoretical. The hydantoin was purified by recrystallization from absolute alcohol and separated, on cooling, in beautiful square tables or blocks, which melted at 175–176° to a clear oil without effervescence.

Analysis (Kjeldahl): Calculated for $C_5H_6O_2N_2S$, : N, 17.71; found, 17.48.

The Action of Potassium Thiocyanate on Acetylglycocoll (Aceturic Acid).—This same 3-acetyl-2-thiohydantoin was also prepared in the following manner: Two grams of aceturic acid and 2.0 grams of dry potassium thiocyanate were suspended in a mixture of 9 cc. of acetic anhydride and 1 cc. of glacial acetic acid and the mixture then heated gently on the steam bath. There was an immediate reaction, the acid and potassium thiocyanate quickly dissolved, and within 5 minutes an orange-colored viscous liquid was obtained. After heating 30 minutes, as in the previous experiment, the liquid was cooled and then poured into cold water. The acetylhydantoin separated at once in yellow prisms. The yield was about 80.0 per cent. of the theoretical. It crystallized from alcohol in blocks and melted at 175–176° to a clear oil. A mixture of this substance with some hydantoin prepared from glycocoll melted at exactly the same temperature.

Analysis (Kjeldahl): Calculated for $C_5H_6O_2N_2S$: N, 17.71; found, 17.73, 17.76.

When this acetylthiohydantoin was heated with an excess of hydrochloric acid it was converted quantitatively into 2-thiohydantoin.[2]

The Action of Potassium Thiocyanate on Hippuric Acid. 3-Benzoyl-2-

[1] *Loc. cit.*

[2] Wheeler, Nicolet and Johnson, *Loc. cit.*

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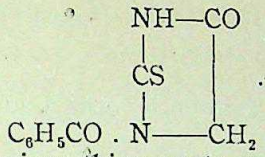
thiohydantoin, 

.—Two grams of hippuric acid and 2.0 grams of potassium thiocyanate were carefully warmed with 9.0 cc. of acetic anhydride and 1 cc. of glacial acetic acid. The anhydride assumed a yellow color and within 5 minutes a perfectly clear orange-colored solution was obtained. There was no apparent loss of thiocyanic acid. After heating at 100° for 30 minutes to complete the reaction, the liquid was cooled and poured into cold water. The hydantoin separated as an oil, which soon solidified. The yield was 86 per cent. of the theoretical. The hydantoin crystallizes from alcohol in square plates, which melt at 165° to a clear oil without effervescence. A mixture of this compound and 3-acetyl-2-thiohydantoin melted at 125–150°.

Analysis (Kjeldahl): Calculated for $C_{10}H_8O_2N_2S$: N, 12.72; found, 12.91, 12.89.

Several experiments were performed in order to determin whether the yield of this thiohydantoin was influenced by the proportions of anhydride and acetic acid used for the condensation. With pure glacial acetic acid there was no evidence of the formation of the benzoylthiohydantoin. Glycocoll likewise gave no 2-thiohydantoin when warmed with potassium thiocyanate in glacial acetic acid. With pure acetic anhydride the yield of benzoylthiohydantoin was much less than when 1 part of acid and 9 parts of anhydride were used. With equal parts of anhydride and acid the benzoylthiohydantoin was formed, but on pouring into water a red oil was always obtained, which showed no signs of crystallizing. In these experiments the yield of the benzoylthiohydantoin was determined indirectly by diluting the solution with strong hydrochloric acid and then evaporating to dryness on the steam bath. The benzoyl group was removed by this treatment and 2-thiohydantoin was formed. The latter was then extracted by alcohol and the potassium salt precipitated by the addition of alcoholic potash. This was then filtered off and weighed. The yields of benzoylthiohydantoin obtained when using different proportions of anhydride and acid are given in the table. In all cases the reaction was carried out with 2 grams of hippuric acid and potassium thiocyanate respectively in 10 grams of the solvent.

TABLE I.

	Acetic anhydride.	Acetic acid.	Yield of benzoylthiohydantoin.
1	..	10	Hippuric acid recovered unaltered.
2	5	5	67 per cent.
3	5	5	52 per cent.
4	9	1	86 per cent.
5	10	..	38 per cent.
6	10	..	40 per cent.

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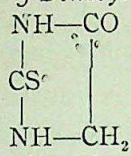
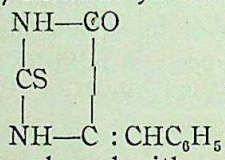
Hydrolysis of 3-Benzoyl-2-thiohydantoin with Hydrochloric Acid. 2-Thiohydantoin,



.—This hydantoin is formed quantitatively by hydrolysis of the above benzoyl derivative with strong hydrochloric acid. After evaporating to dryness on the steambath the thiohydantoin is then purified by crystallization from alcohol. The hydantoin melted with decomposition at 227° and was identical with the thiohydantoin which was prepared by hydrolysis of benzoylthiohydantoic acid.[1]

Condensation of Benzaldehyde with 3-Benzoyl-2-thiohydantoin. 4-Benzal-2-thiohydantoin,[1]



.—Two grams of 3-benzoyl-2-thiohydantoin were condensed with a molecular proportion of benzaldehyde by digestion in glacial acetic acid in the presence of anhydrous sodium acetate. On cooling and pouring into water we obtained 1.6 grams of this benzalthiohydantoin. It melted at 258° and a mixture of this substance with some benzalthiohydantoin, which was prepared by hydrolysis of 1-benzoyl-4-benzalthiohydantoin, melted at the same temperature. Benzoic acid was identified in the acetic acid filtrate.

Analysis (Kjeldahl): Calculated for $C_{10}H_8ON_2S$: N, 1373; found, 13.27.

Action of Acetic Anhydride on 2-Thiohydantoin.—Five-tenths of a gram of 2-thiohydantoin was warmed with 10 cc. of acetic anhydride for exactly 30 minutes. The mixture was then cooled and poured into cold water when a clear solution was obtained. No acetylthiohydantoin separated. The aqueous solution was then evaporated to dryness and the residue obtained crystallized from hot alcohol. Pure thiohydantoin separated on cooling.

NEW HAVEN, CONN.

[FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

STUDIES ON WATER DRINKING. VIII.[2] THE UTILIZATION OF INGESTED FAT UNDER THE INFLUENCE OF COPIOUS AND MODERATE WATER DRINKING WITH MEALS.

H. A. MATTILL AND P. B. HAWK.

Received August 10, 1911.

Introduction.

Current Theories.—Notwithstanding the fact that many persons are

[1] Wheeler, Nicolet and Johnson, *Loc. cit.*

[2] Presented in abstract at the New Haven meeting of the American Society of Biological Chemists, December, 1910; Proceedings, Vol. II, p. xiv. This paper and the

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accustomed to drinking considerable amounts of water with their meals, and with no apparent ill effect, the opinion has been and still is somewhat general, and the statement almost axiomatic, that the use of water with meals is injurious and harmful. The arguments advanced in proof of this statement are typical of that quasi-scientific reasoning which assumes, *a priori*, the truth of certain antecedents; the consequents must therefore logically be true.

A concrete statement of the views as generally held by many in the medical profession and, through them, by the general public, may be cited from Carrington:[1]

"We can lay down the definit and certain rule that it (water) should never be drunk at meals, and preferably not for at least one hour after the meal has been eaten. The effect of drinking water while eating is, first, to artificially moisten the food, thus hindering the normal and healthful flow of saliva and the other digestive juices; secondly, to dilute the various juices to an abnormal extent; and thirdly, to wash the food elements through the stomach and into the intestins before they have had time to become thoroughly liquefied and digested. The effects of this upon the welfare of the whole organism can only be described as direful."

It needs no argument to prove that such effects upon the organism would be direful, but the proof that such effects follow the drinking of water with meals is entirely wanting.[1] On the contrary, experiments have been made which show specifically that certain of these effects do not follow.

1. *The Effect of Water on the Digestive Juices.* *Saliva.*—The degree of dryness of the food determins the amount of saliva poured out upon it, the drier the food the larger the amount of saliva that is secreted.[2] The kind of food introduced into the mouth determins also the physical properties of the saliva. It will be argued, therefore, that the taking of water with food prevents the normal secretion of saliva. In the experi-

two following were presented in abstract before the Second International Congress of Alimentary Hygiene and of the Rational Feeding of Man, Brussels, October, 1910; Proceedings, Vol. I, Section II, p. 30. They were also presented by Mr. Mattill to the Graduate School of the University of Illinois, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[1] Although little experimental evidence substantiates the statement it will be granted at the start, that any circumstance that induces insufficient mastication of the food before swallowing is undesirable, the reason being that salivary digestion in the stomach is not to be overlooked and further, that the movements of the alimentary tract are insufficient to bring about the necessary fineness of division of the food particles. Therefore in all the discussion and experimental work that follows, water with meals means the taking of water when the mouth is empty; the food is masticated, as usual without the aid of water; water is never used to wash down the products of incomplete mastication.

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ments that follow, however, since water is not mixed with the food while this is in the mouth, the effect of water on the secretion of saliva is only a residual one, that is, an effect due to the presence of whatever water may remain in the mouth after swallowing.

Gastric Juice.—The influence of water upon gastric secretion was investigated by Pavlov[2] and Khizhin[3] and still earlier by Heidenhain[3a] and by Sanotskii[3b] and their findings have been confirmed by later investigators, especially by Foster and Lambert.[4] The first mentioned workers in experiments on dogs with Pavlov stomachs and divided vagi showed that water stimulates the flow of gastric juice if comparatively large amounts (400–500 cc.) are ingested, but that with small amounts (100–150 cc.) in half the cases observed, not the least trace of secretion could be found. "It is only a prolonged and widely spread contact of the water with the gastric mucous membrane, which gives a constant and positive result."[3] Since the vagi were divided, the effect of the water must have been that of a chemical excitant. The later investigators[4] in experiments on the influence of water when taken with food showed that water causes not only a more voluminous secretion but also a more acid secretion.

Pancreatic Juice and Bile.—Water also acts as an excitant of pancreatic juice.[5] When 150 cc. of water are introduced into the stomach of a dog the pancreas begins to secrete, or augments its flow, within a few minutes after the water has entered the stomach. Since this amount of water, according to Pavlov, is insufficient to excite a flow of gastric juice, the secretion of pancreatic juice is not secondary to a secretion of the other, but is a direct result of the presence of water in the stomach. In dogs with Pavlov pancreas fistulas Togami[6] has shown that in response to both chemical and psychical stimuli there is evident parallelism between the secretion of gastric juice and of pancreatic juice. Acids of all kinds act as powerful excitants of pancreatic secretion. The flooding of the small intestin with larger amounts of acid chyme means an increased production of pancreatic secretion and a consequent increased flow of pancreatic juice. The biliary secretion has also been shown to respond to pancreatic secretion and the digestive properties of the pancreatic juice are augmented in a very marked way by the bile. Hence the increased acidity of the gastric contents as a result of the stimulating action of water causes a much more active digestive juice to be poured out upon the chyme as it reaches the intestin. Furthermore, certain other experiments from this laboratory have shown increased pancreatic activity[6a] to follow water-drinking with meals, the index being the output of fecal amylase.[7, 7a]

Intestinal Juice.—The effect of water in the intestin has not been demonstrated as clearly as its effect in the middle portion of the alimentary canal. Under ordinary circumstances the intestinal juice is secreted

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only by those portions of the tube with which the food is in contact. Mechanical stimulation is effective in producing a secretion but it is shown that such secretion is comparatively poor in enzymes and contains only salt and water. When poured out upon food the intestinal juice is rich in enterokinase, but much more powerful stimulants even than food in this regard are the pancreatic enzymes; which one of them is active in this direction is not yet known.

2. *The Effect of Dilution upon Enzyme Activity.*—The reactions brought about by enzymes are like all other chemical reactions in that they are reversible. They do not proceed to completion unless the products of the reaction are removed as formed. In a concentrated solution the point at which the reaction comes to a standstill is reached sooner than in a dilute one, and in many instances the equilibrium of a reaction mixture may be disturbed by dilution; the reaction is forced toward completion if water is added. In the light of this fact the increased activity of gastric juice that has been observed under the influence of water may be due to the effect of dilution fully as much as to the increased acidity that accompanies it.

3. *The Rapidity of the Passage of Food as Affected by Water.*—That water begins to pass the pylorus soon after its ingestion has been shown by von Mering.[8] To a large dog with duodenal fistula 500 cc. of water were given through the mouth; within 25 minutes 495 cc. were collected through the fistula. It is probable that when water ingestion is accompanied by the taking of food the passage of water is somewhat delayed. In the experiments to be described it was shown that the equivalents of from one-half to three fourths of the amount of water ingested during a meal, if this amount was large, may be voided in the urine within 45–90 minutes thereafter. These facts would seem to give some ground for the contention that the food elements might be washed through the stomach and into the intestin before they were properly liquefied and digested.

It has been shown by Cohnheim[8a] however that when the fundus is filled with food material a specific mechanism comes into play after the introduction of liquid. Along the smaller curvature there is formed a trough which connects the antrum pylori with the cardiac opening, and this trough has been demonstrated anatomically by Kaufmann.[8b] In this trough water flows past the bolus of food lying in the stomach without as much as washing any of the exterior away. Even when digestion is at its height and when gastric juice is being secreted in large amounts, almost neutral water is often found leaving the stomach. Cohnheim further states that there is no dilution of the stomach contents by liquid food, and the accurate regulation of the pyloric sphincter is not disturbed whether water is taken with the meal or not.

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From the considerations thus briefly reviewed the facts regarding the drinking of water with meals seem to be the following: (1) The ingestion of large amounts of water with meals not only does not hinder the normal flow of digestive juices, but acts as an excitant to their flow; (2) the digestive juices are not made less efficient by dilution; on the contrary, enzyme action is more complete the greater the dilution, within limits; (3) while the food elements might perhaps be washed through the stomach into the intestin more rapidly than is usual (contrary to Cohnheim's belief), yet over against this is the greater amount and efficiency of the digestive juices. The first two conclusions have been substantiated by experiment. The question as to the completeness of the digestion of the food and the degree to which it is utilized under the conditions of greater dilution and supposedly more rapid movement through the alimentary canal has had but little consideration.

The only experimental evidence upon the utilization of the fat of food as influenced by the amount of water taken with meals comes from an investigation by Ruzicka.[9] His conclusions were drawn from data obtained in two experimental periods of two days each, on a bread and meat diet, preceded, separated and followed by a day of milk diet. No attempt was made to have the fat intake uniform from day to day. During the first period water was taken at times and in amounts found desirable, except that none was taken during or immediately following a meal. In the second period approximately the same amount of water was ingested but it was taken during and immediately following the meals. The feces data include dry matter, nitrogen, fat, ash, and carbohydrate by difference. Simple ether extraction was employed in determining fat. The balance of utilization was 94.5 per cent. in the first period as against 95.1 per cent. in the second. The author draws the negative conclusion that a moderate water ingestion at meal time has no harmful influences on the utilization of the food. He emphasizes the adaptability of the organism and supposes that it is a matter of the rapid absorption of the superfluous water. More specific conclusions than these were hardly justified, since neither diet nor water ingestion was absolutely uniform as to time and amount, the water ingestion being particularly variable; it ranged from 300 to 522 cc. at meal time.

The Feces.—The nature and composition of human feces seems generally to be misunderstood. A recent statement is that the feces are chiefly the unabsorbed residues of intestinal excretions.[10] Another statement is to the effect that the feces consist chiefly of bacteria.[10a] A microscopical examination easily shows, however, that these claims are not true. The composition of feces as given by Schmidt and Strasburger[11] is as follows:

(1) Indigestible material in the food.

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(2) Undigested material, which has for some reason escaped the action of the digestive juices.

(3) Residues of the digestive juices.

(4) Bacteria and the products of fermentation and putrefaction.

(5) Products of the epithelial wall, such as decayed cells, leucocytes, etc.

Fats are almost always found in feces, the amount being increased by an increase in the fats in the food. In addition to the food as a source of fat are the digestive juices and the cells of the alimentary epithelia which contain both fats and lipoids.

Many investigators believe that the percentage utilization of a given foodstuff in an available diet is a subject whose importance has been exaggerated. It is said that the percentage differences are so small as to be inconsiderable, particularly in view of the fact that only small quantities of a given substance are involved. Perhaps from the standpoint of the mere existence of the organism this may be true, but the question of continued efficiency is not a negligible one. It seemed probable, at least, that an examination of the feces with regard to their content of fat might give an indication as to the efficiency with which the fat of the food was digested under the influence of water ingestion with meals.

Description.

General Plan.—The general plan of these experiments was to determin in a preliminary period the digestibility of fat in subjects living on a uniform diet. During a second period, with no change in diet, a given volume of water was to be added to that taken normally with each meal, and in a final period the conditions of the preliminary period should again obtain.

The subjects of the experiments were normal men, on the staff of assistants in the Department of Chemistry. The daily periods began and ended at 7 A.M., and the program was as follows: Body weights were taken at 7 A.M., after urinating and defecating. So regular the routine became that in only two or three instances throughout the eight to nine weeks of the experiments defecation did not come at this time. To insure accuracy, body weights were always taken without clothing. The morning meal was taken at 7.30, the noon meal at 12 or 12.15, and the evening meal at 5.30 or 5.45. The three meals were identical and consisted of graham crackers, butter, peanut butter, milk and water. Smaller quantities of water were taken at stated hours during the day. The men went about their duties as usual throughout the day and evening.

The urine was collected in 24-hour samples, the last portion being that passed before weighing in the morning. The urine was analyzed for total

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nitrogen, ammonia, urea, creatinine, creatine,[11a] total and ethereal sulfates, and indican.[11b]

The analysis of the feces was made on each individual stool. As passed it was weighed and thoroughly mixed until uniform throughout. The samples for analysis were then weighed out as quickly as possible to prevent loss by evaporation, which is very rapid. Charcoal was used as a "marker" to facilitate the separation of the feces of different periods; where the uniformity of the diet is not to be interfered with this method is the most satisfactory. One or two capsules (0.2 gram) of finely divided charcoal were taken before breakfast on the day beginning a new period. With but few exceptions the separations thus obtained were very distinct and entirely satisfactory.

The length of time between the taking of food and the appearance of the feces therefrom has been variously given. A recent statement is that particles fed to a man are not usually passed in his feces for two or three days.[10] The observations of the present experiments support the opinion as given by Strasburger[13] that normally this period is 24 hours. Throughout these experiments the charcoal given on one morning appeared in the last portions of the feces passed the next morning, in all but two cases, in both of which the separations were from an ordinary mixed diet, that is, at the beginning or at the end of the experiment.

Methods.—All analyses were made on fresh feces without previous drying, and were always made in duplicate unless the amount of material available was not sufficient. The analysis of the fresh stool[12] to our mind is the ideal method of feces examination. Certainly in view of Shimidzu's findings, mentioned below, we can place no dependence upon data obtained from the analysis of the dried sample.[13a] The analysis of each individual stool in the fresh condition of course demands the expenditure of much more time and energy than are necessitated in the analysis of composit samples of dried feces. However, the added accuracy and the greater value of the data obtained by means of the "fresh" procedure certainly warrant the extra effort.

The method selected for the determination of fat was that proposed and developed by Kumagawa and Suto[14] with the modifications added by Inaba.[15] This method, above all others, yields a product that can be considered to be more nearly pure fat than that yielded by any other methods of extraction.[1] The method as described by its authors is carried out upon air-dried materials but for our determinations no air-drying was employed. Shimidzu[15a] has shown that the drying of tissues on the

[1] This statement does not apply to the method of Folin and Wentworth (*J. Biol. Chem.*, 7, 421–6 (1910)), with which we have had no experience. It appeared after the completion of this work.

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water bath previous to the determination of their fat content by this method causes a loss of fat which may exceed 10 per cent. The loss is probably due to oxidation. It is probable, therefore, that in the determination of fat in feces by this method, the use of fresh material without previous drying yields most accurate results. The procedure involves the saponification of 5–10 grams of fresh feces by a 5 *N* sodium hydroxide solution for several hours; this is overneutralized with 20 per cent. hydrochloric acid, taking care to keep the mixture from becoming hot, and the acid liquid is extracted with ether. Any precipitate remaining is dissolved in hot normal sodium hydroxide, heated for about 15 minutes and extracted with ether; the acid aqueous solution that was first drained off is added and all the fat and fatty acid remaining go over into the ether portion. The combined ethers are evaporated, the residue purified by absolute ether and lastly by petroleum ether, and dried at 60° to constant weight. The fatty acids so obtained were crystallin and almost colorless; care in preventing overheating during the first neutralization and a sufficient drying of the last ether residue before taking up in petroleum ether are essential to obtaining them in pure form.

It is evident that by this method the unsaponifiable substances are determined along with the fatty acid and the authors[14] give a satisfactory procedure by which these may be determined. It was shown by Inaba[15] that the unsaponifiable substances in the feces amount to about 10 per cent. of the total fatty acids determined and that a separation of these substances is of importance, if most accurate results are desired. Inasmuch as a uniform diet was fed in these experiments, any difference in the fat content of the feces from one period to another was probably subject to no correction on this account.

Experiments on Copious Water Drinking with Meals.

General Description.—The first experiments on Subjects H and W may now be considered in detail. Subject H was a tall well-proportioned man weighing 70.22 kilograms at the beginning of the experiment. He had been on a diet of comparatively simple variety and as he was not fond of milk and drank neither tea nor coffee, water comprized the chief liquid portion of his diet. Subject W was of smaller stature and weighed 63.2 kilograms at the beginning of the experiment. He was accustomed to the diet as offered by a club table of the better grade and usually drank water sparingly. He regularly smoked a cigar after the evening meal and did so throughout the experiment. Both subjects were put upon the same uniform diet of graham crackers, butter, peanut butter and milk. It contained 180 grams of fat per day distributed for each food and meal as follows:

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	Amount.	Fat.
Oatmeal crackers.....	150 grams	11.7 grams
Peanut butter.....	20	9.2
Butter.....	25	21.1
Milk.....	450 (cc.)	18.0
Water.....	100 cc.	....
		Total, 60.0

In addition, 200 cc. of water were taken at 10 A.M., at 3 P.M., and again in the evening or just before retiring, making a total of 900 cc. of water per day during the three-day preliminary period.[1] On the morning of the fourth day before breakfast charcoal was taken and during the five days following one liter of water was added to the menu of each meal, making 1100 cc. per meal and a total of 3900 cc. per day. On this diet both subjects record a feeling of fulness that sometimes became temporarily slightly uncomfortable. It was necessary to urinate frequently especially during the first few hours after the meal; for a short time after eating there was a desire to remain quiet and inactive, as is the case after any full meal; within three-quarters of an hour or an hour, approximately half the water taken at the meal was voided. Both subjects record that the feeling of fulness and lassitude noted immediately after meals became less marked after the second day of the water period. Both felt perfectly well at all times and had normal appetites. After the fourth day H records that he did not notice the feeling of fulness which followed the high water ingestion of the first few days of the water period.

The period of copious water ingestion lasted five days. On the morning of the sixth day charcoal capsules were taken before breakfast and during that and the two following days the diet of the preliminary period was resumed. The experiment ended with the taking of charcoal on the morning of the fourth day of this period.

Discussion of Results.—The data upon the excretion of fat in the feces during these three periods are given in Tables I and II.

Subject H, Table I.—The data show that the average daily excretion of fat during the preliminary period was 8.37 grams, during the water period 7.16 grams and 9.22 grams during the final period. The digestion and absorption of fat were seemingly more complete during the water period than during the preliminary period and upon the withdrawal of water the excretion of fat rose to an amount that was higher than before the period of water ingestion. A slight gain in weight was recorded,

[1] The water supply (see Fowler and Hawk, *J. Exp. Med.*, 12, 390 (1910)) of this community is from deep wells and for use in these experiments it was softened by the addition of five liters of saturated lime water to thirty liters of the tap water. After standing several hours or a day the precipitate was filtered off. This water had an agreeable taste; its alkalinity was 70 to phenolphthalein, 180 to methyl orange, and its hardness determined by soap solution was 92 parts per million.

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70.29 kilograms on the morning of the first day of water and 70.88 kilograms on the morning of the first day after the water. This gain of 600 grams was not lost for at least three months thereafter.

TABLE I.—SUBJECT H.

Preliminary period. 3 days.		Water period. 5 days.		Final period. 3 days.	
Number of stool.[1]	Fat.	Number of stool.[1]	Fat.	Number of stool.[1]	Fat.
1	3.23	5	2.16	10	6.06
2	5.16	6	5.65	11	2.14
3	9.73	7	3.58	12	8.79
4	7.00	8	16.59	13	10.68
Total	25.12	9	7.80	Total	27.67
Average	8.37	Total	35.78	Average	9.22
		Average	7.16		

TABLE II.—SUBJECT W.

Preliminary period. 3 days.		Water period. 5 days.		Final period. 3 days.	
Number of stool.	Fat.	Number of stool.	Fat.	Number of stool.	Fat.
1	9.22	5	5.80	11	5.56
2	10.60	6	1.31	12	7.76
3	3.85	7	5.98	13	1.84
4	7.00	8	6.41	14	6.34
Total	30.67	9	7.01	Total	21.50
Average	10.22	10	2.64	Average	7.17
		Total	29.15		
		Average	5.83		

Subject W, Table II.—During the preliminary period there was an average daily excretion of 10.22 grams of fat in the feces. During the water period this was reduced to an average of 5.83 grams per day and in the final period it rose to 7.17 grams per day, an amount only slightly above that of the water period. From these data it would appear that during the period of copious water drinking the fats of the food were more completely digested and absorbed than either before or after this period and that this effect of the water drinking was not temporary but more or less permanent. In the case of W also a slight gain in weight accompanied the experiment. On the morning of the first day of water his weight was 63.46 kilograms; at the end of this period it was 64.16 kilograms. This gain of 700 grams might be attributed to retained water, except for the fact that it was not lost subsequently. After the lapse of three months, during which time the subject was on an ordinary mixed diet, his weight was identically the same as at the end of the water period of this experiment. While great significance can not be attached to so small a change in weight, even granted that it is not due to water, it must nevertheless be borne in mind that the diet throughout the experiment was absolutely uniform with the exception of the water ingestion.

[1] Weights of all stools are included in the third paper of the series.

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It seemed reasonable to assume that the decreased excretion of fat during the water period was due to more complete utilization as a result of the large volumes of water ingested, and several explanations could be suggested. Of first importance was the direct stimulating effect of water upon the digestive juices. In his first experiments on dogs Pavlov[3] found that a large amount of water (500 cc.) caused a flow of gastric juice, while a small amount (150 cc.) in half the cases observed had not the least effect. He states that the important factor is a prolonged and widely spread contact of water with the gastric mucous membrane. This contact can hardly be called prolonged because of the rapid passage of water through the pylorus; this very circumstance, however, might make a large volume of water effective as against a small volume in that the former did secure a more widely spread contact than the latter, and perhaps also for a slightly longer period of time. To obtain further information on this point it was considered worth while to make another experiment upon the effect of a smaller amount of water taken with meals, but whose use should extend over a longer period of time.

Experiments on Moderate Water Drinking with Meals.

Description, Methods, Etc.—The plan of the experiment was exactly the same as that of the previous one. Two subjects were maintained on a uniform diet of small water content for several days. Then during a period of ten days in which the same diet was continued, 500 cc. of water in addition to the usual amount were taken with each meal. In the final period the conditions of the preliminary period were again in force. The daily routine was the same as in the preceding experiment. Charcoal was used to separate the feces of the different periods and the analyses were made on each individual stool in a fresh condition.

After an interval of about three months W, of the preceding experiment, again served as subject. In the meantime he had been at the same table as before, had had much the same kind of food, and in general the same dietary habits with the exception that he had formed the habit of taking more water with his meals than before the first experiment. His weight at the beginning of this experiment was 64.18 kilograms, almost exactly the same as at the end of the first experiment.

Subject E was of the average build and weighed 73.6 kilograms. His habits of eating were irregular. During the previous year he had for a time lived on one substantial lunch-counter meal a day,[1] later on two, and during the months preceding the experiment on three at a regular table. He was accustomed, ordinarily, to taking considerable amounts of water with his meals.

The food of each meal, and its fat content were as shown:

[1] Howe, Mattill and Hawk, This Journal, 33, 570 (1911).

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(In grams.)	Amount.	Fat.
Oatmeal crackers	150	12.9
Peanut butter	20	9.2
Butter	25	21.1
Milk	400 (cc.)	16.0
Water	100 cc.	
	Total,	59.2

The diet of W was slightly reduced from what it had been before and was as follows:

(In grams.)	Amount.	Fat.
Oatmeal crackers	125	10.8
Peanut butter	20	9.2
Butter	25	21.1
Milk	400 (cc.)	16.0
Water	100 cc.	
	Total,	57.1

In addition, each man took 200 cc. of water at 10 A.M., at 3 and at 8.30 P.M., making a total water ingestion of 900 cc. per day during the preliminary period. During the water period the addition of 500 cc. of water to each meal made the total water ingestion 2400 cc. per day during that time.

Discussion of Results. Subject W.—On the diet as given, some little difficulty was experienced in obtaining nitrogen equilibrium in the preliminary period. Charcoal was taken on the morning of the eighth day, but for the sake of keeping uniformity in the feces data it seemed best not to change the diet. Six days passed and on the morning of the fourteenth day charcoal was again taken and water added to the regular diet. The separation of the preliminary period into two parts proved to be a very important incident in view of what the feces data show (Table III).

TABLE III.—SUBJECT W.

I. Preliminary period. 7 days.		II. Preliminary period. 6 days.		Water period. 10 days.		Final period. 5 days.	
Number of stool.	Fat.	Number of stool.	Fat.	Number of stool.	Fat.	Number of stool.	Fat.
1	12.30	7	4.20	14	1.84	24	3.54
2	3.19	8	7.47	15	10.18	25	6.58
3	4.23	9	8.07	16	4.70	26	3.36
4	4.71	10	10.52	17	9.70	27	8.56
5	12.20	11	3.21	18	3.89	28	5.54
6	5.06	12	5.97	19	7.54	29	4.08
Total	41.69	13	1.90	20	1.74	Total	31.66
Average	5.96	Total	41.24	21	11.59	Average	6.33
		Average	6.89	22	7.85		
				23	8.72		
				Total	67.75		
				Average	6.78		

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During the time that intervened between his two experiments Subject W, as has been mentioned, while on an ordinary mixed diet, continued the habit of taking considerable water with his meals. As is evident from the diet of the preliminary period the amount of water taken was small and was, in fact, much less than he was accustomed to use. While this restricted amount of water did not immediately make itself felt in the first few days of the experiment, it did begin to show in the latter part of the preliminary period by a seemingly less complete digestion and absorption of fat. This is evident in an increase in the average daily fecal output of fat during the second part of the preliminary period. The average daily amount of fat excreted in the first part of this period was 5.96 grams as against 6.89 grams in the second part. Since the charcoal separation of this preliminary period into two portions was clear and definit this increase in fat in the feces during the latter part seems to mean a less efficient digestion and utilization of the fat of the food. That this evidence did not appear until some days after the amount of water had been reduced indicates, as in the first experiment, that the beneficial effect which water had upon digestion and absorption did not cease with the withdrawal of water, but was more or less permanent beyond the time during which water was taken with the meals. The evidence given by this finding was entirely unlooked for and seems to be of great importance.

Attention should also be called to the comparison of the fat data of this preliminary period with those of the preliminary period of the first experiment, Table II. The average daily amount of fat excreted in the preliminary period of the first experiment was 10.22 grams as against 5.96 in the second. The average percentage utilization of fat in the former was 94.3 per cent. as against 96.5 per cent. in the latter. These data showing so pronounced an improvement in the digestion and utilization of fat are on an individual living on the same kind of food, but separated by a period of three months in which water drinking with meals was practiced. From these results the conclusion as to the effect of water drinking with meals upon the utilization of fat is further strengthened.

It is further seen in Table III that the average daily excretion of fat in the preliminary period, 6.89 grams, suffered but little change in the water period, 6.78 grams, but was slightly decreased, 6.33 grams, in the final period. Just why this decrease should have come in the final period rather than during the water period is not clear. Perhaps there is a lag in the appearance of the results of water drinking, just as it has been shown that its effects are more or less permanent. In this case the moderate amount of water may have had a stimulatory effect that was not evident during the water period but made itself felt during the period following. The question of individuality probably enters in also. From

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a study of the data on Subject W during this experiment it may be concluded that the effect of moderate water-drinking with meals upon digestion is in the same direction as that of copious water drinking but somewhat less marked.

Subject E.—An examination of Table IV shows the variations in fat excretion from one period to another to be small although similar to those obtained before. The output of fat fell from 6.61 grams per day in the preliminary period to 6.39 grams per day under the influence of moderate water drinking, and again rose to 6.70 in the final period.

Again it appears that the effect of drinking water in moderate amounts with meals is in the same direction as when large amounts are used, although the differences observed are of a smaller order of magnitude; as with the copious amounts, absolutely no harmful effects were to be observed. With moderate amounts of water the inconvenience of disposing of an unusual quantity of liquid after the meal was removed, and the lethargic effects of a full meal, such as were noted under the experiment on copious water drinking, were also avoided.

TABLE IV.—SUBJECT E.

Preliminary period. 7 days.		Water period. 10 days		Final period. 4 days.	
Number of stool.	Fat.	Number of stool.	Fat.	Number of stool.	Fat.
1	3.79	9	3.33	20	2.79
2	1.51	10	5.85	21	5.60
3	8.96	11	3.96	22	7.75
4	11.63	12	8.20	23	7.88
5	3.92	13	9.78	24	2.77
6	8.66	14	6.50		
7	5.20	15	7.07	Total	26.79
8	2.63	16	3.63	Average	6.70
		17	2.90		
Total	46.30	18	9.59		
Average	6.61	19	3.10		
		Total	63.91		
		Average	6.39		

The results just given were obtained on subjects one of whom (W) had lately become accustomed to drinking with meals; the other of whom (E) habitually took considerable water with his meals. In each case the organism, though accustomed to the presence of water in the alimentary tract during digestion, responded to an increase in its amount by a better utilization of the fat of the food. The results obtained, therefore, probably represent the minimum rather than the maximum effect that may be obtained by moderate water drinking with meals, and are such as might safely be expected in any individual, but especially in one not accustomed to drinking water under these conditions.

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The Effect of Copious Water Drinking with Meals upon an Habitual Water Drinker.

At this point an answer was sought to the question as to whether a very large water ingestion with meals would show its effect upon digestion even though relatively large amounts of water were habitually taken at meal time. For this investigation Subject E seemed very well fitted; during the experiment on moderate water drinking he had frequently made it his boast that he was not drinking more water with his meals during the water period than was his custom. It seemed advizable therefore to try upon E the effect of such amounts of water as would be copious for his digestive mechanism.

Description.—Continuing with the same diet as in the final period of the previous experiment, a period of six days was made the preliminary period for this experiment. During the five days following this period an addition of one and one-third liters of water was made to the water ingestion of each meal. This is a larger amount of water than was used in the first experiment on copious water drinking, where only 1000 cc. additional were taken with each meal. A final period of three days closed the experiment. On the very first day of this large water ingestion Subject E records that he had no trouble in drinking all of the water, nor was any discomfort experienced throughout the experiment.

TABLE V.—SUBJECT E.

Preliminary period. 6 days.		Water period. 5 days.		Final period. 3 days.	
Number of stool.	Fat.	Number of stool.	Fat.	Number of stool.	Fat.
1	2.75	8	3.17	14	5.58
2	4.28	9	1.84	15	3.87
3	10.87	10	11.35	16	8.69
4	5.90	11	4.46	17	0.82
5	7.44	12	7.33		
6	8.59	13	3.53	Total	18.96
7	1.97			Average	6.24
Total	41.80	Total	31.68		
Average	6.97	Average	6.34		

Discussion of Results.—Table V shows that the average daily excretion of fat in the preliminary period, 6.97 grams, fell to 6.34 grams in the water period, and the daily average value for the final period, 6.24 grams, was even slightly less than for the water period. The effect of copious water drinking with meals is seen to be in the same direction when the organism is accustomed to water drinking as when it is not, except that when water drinking with meals is habitual the results are less striking than otherwise.

Inferences and Discussion.

All of the observations made have pointed to a decreased elimination of fat in the feces when water was taken with meals, indicating a more

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complete utilization of the fat of the food than without the water ingestion, and in most instances the evident better digestion continued for several days beyond the period during which an increased water ingestion was practiced. A large amount of water was more efficient in this regard than a small one and a more pronounced result was obtained in persons not used to water drinking with meals than in those for whom it was habitual.

The results of our experiments warrant more than a negative conclusion. The ingestion of water along with the food secures a better utilization of the fat of the food as shown by a diminished excretion of fat in the feces. It is possible to explain this result on the basis of four different facts.

(1) The Stimulating Action of Water upon the Gastric Secretion and Independently upon the Secretion of Pancreatic Juice and Bile.

The facts observed by Pavlov and his co-workers[3] mentioned above, and the findings of Foster and Lambert[4] as to the stimulating action of water upon the gastric secretion in dogs have also been observed in human beings with gastric and esophageal fistulas. In some of the older investigations it was shown[16, 17, 18] that a purely psychic secretion, such as is noted in dogs, is not as pronounced in man as in these animals. A pleasant taste of food in the mouth caused a flow of gastric juice in some instances, but whether, in general, such a secretion of gastric juice in man arizes indirectly through stimulation carried by the blood or by the nerves, or whether it is due directly to the contact of substances with the mucous membrane of the stomach is uncertain. The observations of Bogen,[19] Kaznelson,[20] and Sommerfeld[21] upon patients with gastric fistulas have clearly demonstrated a psychic secretion. Most varied stimuli through taste, smell, and sight of food, and through sounds associated with the preparation of food called forth a secretion of gastric juice. In the subject examined by Lavenson[22] no psychic secretion was demonstrable but water was found to be a definit though not powerful stimulus. Sommerfeld[21] was able to show that water had a stimulating action upon the gastric secretion, and further, that the mere drinking of water, after the manner of sham feeding, caused a flow of gastric juice. It is claimed that saliva is not a factor in inducing gastric secretion. The evidence adduced by Hemmeter[23] as to a salivary hormone producing increased flow of gastric juice could not be verified by Loevenhart and Hooker.[24] The stimulating factor may be mastication itself, including the taste phenomena and also the desirability of the food.

In human beings as well as in the lower animals investigated the acidity of the gastric juice is found to vary with the kind of food. The findings of Foster and Lambert[4] on dogs with accessory stomach indicate not only

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a more voluminous but also a more acid secretion when water is taken with food and they suggest an automatic control in the stomach, such that the chyme, no matter what its state of dilution, always has the same optimum acid concentration. The increased acidity noted in the accessory pouch may not actually exist in the stomach proper; here, by dilution, the acid concentration may remain unchanged. Certain other experiments reported from this laboratory[24a] apparently confirm this view. If the stimulation of water is entirely a chemical one, however, it is difficult to see why the mucosa of the pouch, which is not in contact with the water, should respond as readily as the stomach itself, even though it has the same nerve and blood supply. Any effect which the accessory pouch shows may possibly be less marked than the one actually secured in the stomach proper.

Whether an increased acidity and digestive power of the gastric juice is of immediate importance in the digestion of fat is not clear. The cleavage of fat by gastric lipase is very minimal in the normal acid reaction of the stomach except when the fats are in the form of a natural emulsion. London and Versilova[25] showed that in dogs the cleavage of fat fed in such a form (egg-yolk) rose as high as 32 per cent. in the stomach, due in part to gastric lipase and in part to regurgitated duodenal juice. A similar observation has been made recently by Levites.[26] Kaznelson[20] found a lipase in the gastric juice of her patient. According to Lavenson's observations[22] a regurgitation of bile and pancreatic juice in the stomach occurred with great constancy when oil was given.

No absorption of fat takes place in the stomach. In the experiments of London and Versilova[25] where one-third of the fat administered was split in the stomach no absorption took place until this material reached the ileum. As a result of their findings Camus and Nicloux[27] and also Stire[28] emphasize the unimportance of gastric lipase. The fats undergo practically no change in the stomach, and when they do it is as a result of a regurgitated duodenal secretion.

In view of these facts the importance, for fat digestion, of the greater quantity of gastric juice, or a greater acidity, or both, as a result of the stimulating action of water with the food is to be sought rather in the effect upon the secretion of the bile and the pancreatic juice.

(2) The Acid Chyme as an Excitant for the Flow of Pancreatic Juice and Bile.

The formation of secretin from prosecretin is the result of an acid reaction of the duodenum; the larger the amount of acid the greater the stimulation given to the secretory action of the pancreas, and the flow of bile is regulated by the same mechanism. That the efficiency of bile in aiding the digestion of fats by pancreatic lipase is due to the bile acids

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has again been shown recently by Terroine.[29] The same investigator has also shown[30] that at an optimum concentration of pancreatic juice and of esters or whatever other substances are undergoing cleavage, the hydrolysis is activated proportionately by increasing quantities of bile salts.

Fat in small amounts is a regular constituent of pancreatic juice and especially of the bile, and an increase in these secretions should cause increased elimination of fat in the feces unless a compensation was found. This increased excretion is not found, but, on the contrary, a constant *decrease* is observed under the influence of water drinking with meals. It follows from this that the digestibility of fat during the period of water drinking with meals was increased even beyond what the data indicate, since part of the excreted fat might come from the larger amounts of digestive juices secreted under the stimulating influence of water. And furthermore inasmuch as the fat values for the stools derived by the Kumagawa-Suto technic include any cholesterol present, the increased output of biliary cholesterol during the water period would also be a factor tending toward an apparently augmented output of fecal fat during this interval.

(3) Heightened Peristalsis and Increased Blood Pressure as Factors in the More Complete Digestion and Utilization of Fat.

Peristalsis is known to increase with the volume of material within the intestin. Whether a large amount of a liquid mass is as efficient in this regard as an equal bulk containing less water is uncertain. The effect of dilution and increased peristalsis brought on by purgatives was shown by Ury[31] not to increase the amount of soluble foodstuffs or of their products in the feces. His observations were limited to soluble protein and to sugar.

Water begins to pass the pylorus very soon after its ingestion, and is quickly absorbed. During the time that this water is in the tissues and is flowing in the blood stream, the increased volume causes a rise in blood pressure similar to the rise regularly following a meal. In duplicate feeding experiments on a dog with gastric fistula Dobrovolskii[32] found that after bleeding there was an almost complete stoppage of the process of digestion during the first 3 hours, due in part to the decreased blood pressure. No measurements of blood pressure were made during these experiments on water drinking; it seems reasonable to assume, however, that a greater blood pressure and a consequent stronger and more rapid heart beat might also be factors in the more complete absorption of the fat of the food when water is taken with meals.

Both of these factors, peristalsis and blood pressure, are to be investigated as to the effect which large volumes of water with meals have upon them.

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(4) Dilution as a Factor in More Complete Utilization.

More important than any of the other factors, probably, is this one of dilution. Like all other chemical reactions, those brought about by enzymes are reversible. Governing these is the general principle expressed in LeChatelier's theorem which states that when a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place within the system which opposes the constraint, *i. e.*, one by which its effect tends to be destroyed. Processes within the system tend to counteract the effect of external changes. Thus the dilution of any solution in which the reaction $AB \rightleftharpoons A + B$ had come to equilibrium would result in the formation of further amounts of A and B in order to increase the total concentration of dissolved material by way of counteracting the effect of dilution. The reaction would be driven toward the right and would be brought more nearly to completion. Looked at in another way such a reversible reaction as given above reaches an equilibrium whose constant is expressed by the equation $C_a \times C_b / C_{ab} = K$. The numerical value of this fraction as expressed by K remains unchanged whatever the total concentration of the solution may be. If the solution is diluted, causing a reduction in all three of the terms C_a, C_b and C_{ab}, the values C_a and C_b must diminish relatively less rapidly than C_{ab} in order that K should remain the same. And in order to accomplish this some of the substance whose concentration is C_{ab} is transformed into the substances whose concentrations are C_a and C_b. A concentrating of the solution would have the opposit effect. Now all of the hydrolytic cleavages occurring in digestion are of the type $AB \rightleftharpoons A + B$, *i. e.*, a single substance is broken up into two or more products, and such reactions are brought the more nearly to completion the greater the dilution in which they take place. The corresponding synthetic reactions are accomplished by beginning with a high concentration of the corresponding decomposition products.

The failure to provide for the removal of the end-products, either by dilution or by dialysis, has often been shown to prevent a reaction from going to completion. In experiments upon the saponification of fats by pancreatic juice obtained by fistula from a dog Terroine showed[33] that the addition of oleic acid or of sodium oleate to olein emulsions rendered saponification of the latter more difficult. The addition of glycerol to suspensions of olive, castor, and cottonseed oils had the contrary effect of making them much more readily saponifiable, but this was due to the physical effect of the glycerol in making the emulsions more complete and more permanent by virtue of decreasing the surface tension. In his investigations upon human pancreatic juice Bradley[34] found that the undiluted juice acted on ethyl butyrate less rapidly than when diluted

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1 : 10. The optimum dilution was found to lie between 1 : 15 and 1 : 20. In experiments on the effect of bile salts on pancreatic juice Terroine[35] found that the action was a physico-chemical one, directly upon pancreatic juice, that if the time of the action was prolonged digestion was retarded, and that if still more prolonged digestion was inhibited. Shorter periods resulted in maximum digestion.

In the light of these facts the better absorption and more complete utilization of the fats attendant upon water ingestion with meals are a result of the greater completeness of the hydrolytic cleavage under the influence of dilution and of the accompanying more rapid removal of the end-products.

Summary.

Experiments were performed on men living on a uniform diet; a preliminary period of small water ingestion was followed by a period of large water ingestion with meals, and this, in turn, by a final period with the original conditions.

When one liter of water additional was taken with meals the average daily excretion of fat in the feces was much reduced below that found when a minimum amount of water was taken with meals; one and one-third liters had a like effect; a similar but less marked reduction was observed when 500 cc. of water were taken with meals.

The decreased excretion of fat observed during water drinking with meals was usually evident for a number of days after water had ceased to be taken in large or moderate amounts with meals indicating that the beneficial influence of water was not temporary but was more or less permanent.

A slight gain in weight accompanied the water drinking and this gain was not subsequently lost.

After several months of moderate water drinking with meals a pronounced improvement in the digestibility of fat was observed, the percentage utilization having risen from 94.3 to 96.5.

The better digestion and absorption of fat was probably due to the following factors:

(1) Increased secretion of gastric juice and independently of pancreatic juice as a result of the stimulating action of water.

(2) Increased acidity of the chyme bringing about a more active secretion of pancreatic juice and bile.

(3) Increased peristalsis due to larger volume of material in the intestin and increased blood pressure due to rapidly absorbed water.

(4) A more complete hydrolysis of the fats by lipase due to increased dilution of the medium and consequent more rapid absorption.

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STUDIES ON WATER DRINKING: IX. THE DISTRIBUTION OF BACTERIAL AND OTHER FORMS OF FECAL NITROGEN AND THE UTILIZATION OF INGESTED PROTEIN UNDER THE INFLUENCE OF COPIOUS AND MODERATE WATER DRINKING WITH MEALS.

BY H. A. MATTILL AND P. B. HAWK.

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Introduction.

By far the larger part of the organic material eliminated in the feces is of unknown nature and composition. A knowledge of the source of fecal material is thereby made the more difficult to obtain. Three sources are usually considered as contributing to the nitrogenous material excreted as feces: (1) food residues, (2) residues of the digestive juices and cellular material from the intestinal wall, (3) bacteria and their products. Each of these in turn has been emphasized as the principal contributing agent, but no attempt seems ever to have been made to determin the "nitrogen partition" in the feces.

That the food residues of an available diet form any considerable part of the excreted material has had to be denied since the early work of Voit on fasting feces. In feeding experiments on dogs this investigator[1] showed that the amount of nitrogen in the feces was not proportional to the amount of meat fed. No muscle fibers or protein could be detected in the feces. Voit[2] showed that the material produced in an isolated loop of the intestin of a dog was of a similar composition and contained the same amount of nitrogen as the feces of the normal intestin through which food was passing. Prausnitz,[3] in experiments on men, showed that the composition of the feces varied with the diet and gave a definition of normal feces as those resulting from the eating of any food that is completely digested and absorbed. His data also show that the amount of nitrogen in the feces is uninfluenced by the amount in the food, although Schierbeck[4] finds considerable variation in this respect. Rubner[5] found that in man the amount of feces and its nitrogen content are determined entirely by the cellulose content of the diet. In the same way he found that on a milk diet the resulting fecal mass was almost directly proportional to the quantity of milk ingested.

It is entirely probable that on a diet whose constituents are not entirely available the amount of feces is increased by the undigested cellulose, and the nitrogen content is increased by the larger amount of digestive juices secreted because of the larger volume of food and the accompanying increased peristalsis.

About one-third of the dry matter of human feces consists of bacteria, and at least one-half of the nitrogen of feces is bacterial in its origin.[6,7,8]

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Little is known as to the conditions upon which the growth of the intestinal flora depends. In herbivora, whose food materials contain large amounts of cellulose, the presence of organisms that bring about the decomposition and utilization of this substance is an advantage. Even so, only 45 per cent. of the energy of such food is utilized. In the intestin of carnivora the existing micro-organisms are limited to unabsorbed protein and the residue of the digestive juices for their food supply. In man, living upon a diet that contains food material of both the available and the unavailable kind, a condition midway between might be expected, just as the relative length of the intestin lies between that of herbivora and carnivora.

A recent claim of Schottelius[11] is that the presence of bacteria in the intestin of vertebrates is a desirable condition. Among their functions are the following: to prepare the food for absorption, to stimulate peristalsis, to inhibit the growth of pathogenic bacteria, and to render the body immune to bacterial poisons and to pathogenic organisms in general. The investigations looking toward a determination of the possibility of normal life with a steril alimentary canal have yielded conflicting results;[9,10] the nature of the animal, of its food and its digestive mechanism are all important factors in deciding the question.

Since the supply of nutriment for the bacteria of the lower intestin must consist mainly of the nitrogenous residues of the digestive juices and of the unabsorbed foodstuffs that reach the large intestin, we should expect a decreased bacterial growth when this food supply is decreased. An increase in unabsorbed residues of digestive juices and foodstuffs should result in an increased bacterial growth. It would seem reasonable to suppose, therefore, that any influence leading to the incomplete digestion and absorption of food, especially of its protein portion, in the alimentary tract would result in increased elimination of nitrogen in the feces, or in increased bacterial growth in the lower intestin, or in both of these conditions.

It was thought that evidence on both of these points might be valuable in determining the probable effect of water ingestion with meals.

The only earlier experimental evidence as to the influence of water drinking with meals upon the utilization of food was obtained by Ruzicka[12] in an experiment upon himself. The conditions and routine of his experiment are referred to in the previous paper on the utilization of fat. During the first 2-day period of his experiment when no water was taken with the meals, 118.4 g. protein were ingested, 17.9 g. excreted; during the second 2-day period when water was taken with the meals, 125.9 g. protein were ingested, 16.5 g. excreted. Protein utilization was 84.9 per cent. in the first period and 86.9 per cent. in the second. Neither

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diet nor water ingestion was sufficiently uniform to allow any but the most general conclusions to be drawn.

More specific evidence comes from an investigation made in this laboratory by Fowler and Hawk.[13] Their subject was brought to nitrogen equilibrium on a constant and uniform diet and continuing this diet one liter of water was added to each meal for a time of five days; this was followed by a short final period in which the original conditions held. It appears that the average fecal output per day and the average dry matter per day in the feces were both much less during the water period than during either of the other periods, and that the average amounts during the final period were less than those of the preliminary period. More detailed examination of the feces was confined to the determinations of total and bacterial nitrogen on one stool in each of the three periods. These findings showed that both these forms of nitrogen were much reduced in amount during the period of copious water ingestion and that after water ceased to be used in unusual amounts these values did not immediately return to the values found for the preliminary period but were still lower than those during the final period. The authors concluded that these findings indicated a more economical utilization of the protein of the food. During the water period of five days the subject gained approximately two pounds in weight, and continued to gain for a number of months after the end of the experiment and the return to ordinary mixed diet. It could not be said that the water drinking had no effect, nor that it had an ill effect.

These conclusions as to the digestibility and availability of the foods during water-drinking were based upon analyses of but three stools, one in each of the three periods. The importance of the conclusion reached seemed to justify more extensive experiments along the same line, experiments in which each individual stool of the whole investigation should be subjected to similar examination. The present investigation was therefore planned on this basis.

Description.

General Plan.—The general plan and routine of the experiment has been described in the preceding paper.

Methods.—All analyses were made on fresh feces without previous drying. The samples usually weighed out with the approximate weights were as follows:

(*a*) Two 2-gram samples for total nitrogen.

(*b*) Two 2-gram samples for bacterial nitrogen.

(*c*) Two 2-gram samples for acid-alcohol extract.

Total Nitrogen.—During the earlier experiments dried feces were used for the total nitrogen determinations, with unsatisfactory results due to loss of nitrogen during the drying. That there is such a loss the

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data clearly show; this has been observed before.[14,14a] In the later experiments the determination of total nitrogen was made upon the fresh material with satisfactory results.

Bacterial Nitrogen.—The method for bacterial nitrogen is described in another paper from this laboratory.*

Residue Nitrogen.—As explained more in detail under the determination of bacterial nitrogen, residue nitrogen is that which comes from the well-washed sediments in the sedimentation for bacterial nitrogen. It represents undigested and insoluble nitrogen that occurs in the larger particles of the feces.

Extractive Nitrogen.—The sample for acid-alcohol extract was rubbed up in a small Erlenmeyer flask with a known volume of 95 per cent. ethyl alcohol made 0.2 per cent. acid with hydrochloric acid. The flask was stoppered and was allowed to stand at room temperature for a week, being shaken up at least once each day. Nitrogen was then determined on an aliquot portion (one-half) of the alcohol originally added. This represents such nitrogenous end-products as are below the proteose stage, and the soluble nitrogen of the digestive juices and of the pigments. Almost invariably this amount is less than that obtained by a similar extractive method on the bacterial sample as described under bacterial nitrogen. This may be due to the greater fineness of division that is secured in the case of the latter and perhaps also to the solvent action of the 0.2 per cent. hydrochloric acid used in making the bacterial suspensions.

All determinations of nitrogen of whatever form were made by the Kjeldahl method. Instead of metallic mercury, copper sulfate was used as catalyst in the digestion.

Experiments on Copious Water Drinking with Meals.

As mentioned before, subjects H and W were put on the same diet; the amounts had to be altered before nitrogen equilibrium was reached. The quantity and composition as finally given were as follows:

	Amount (per meal).	Nitrogen.
Graham crackers	150 grams	2.087 grams
Peanut butter	20 "	0.882 "
Butter	25 "	0.020 "
Milk	450 (cc.)	2.360 "
		Total 5.349
Protein		33.44 grams
Protein per day		100.32

On this diet a condition of nitrogen equilibrium was attained approx-

* Mattill and Hawk, *J. Exp. Med.*, 14, 433 (1911).

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imately at the end of the third day. The exact nitrogen balance may be seen from the following:

Subject H.	Nitrogen in feces	2.153
	Nitrogen in urine	14.036
	Nitrogen in excreta	16.189
	Nitrogen in food	16.046
		—0.143
Subject W.	Nitrogen in feces	2.385
	Nitrogen in urine	14.534
	Nitrogen in excreta	16.919
	Nitrogen in food	16.047
		—0.873

TABLE I.—SUBJECT W.

	Number of stool.	Nitrogen distribution. Fecal nitrogen (det.).	Fecal nitrogen (calc.).	Bacterial + soluble nitrogen.	Bacterial nitrogen.	0.2 per cent. HCl-soluble nitrogen.	Acid-alc.-soluble nitrogen.	Percentage of total fecal nitrogen found in. Bacterial.	HCl-soluble.	Acid-alc.-soluble.
Preliminary period. 3 days.	1	1.738	1.911	1.737			0.445			23.3
	2	2.333	2.536	2.305			0.599			23.6
	3	0.913	0.961	0.874			0.193			20.1
	4	1.649	1.747	1.588			0.586			33.5
	Total	6.633	7.155	6.504			1.823			
	Average	2.211	2.385	2.168	1.279 (calc.)	0.889 (calc.)	0.608			25.5
Water period. 5 days.	5		(1.387)	1.296			0.280			15.2
	6	0.301	0.287	0.268			0.085			28.2
	7	1.337	1.433	1.339			0.416			29.0
	8	1.499	1.593	1.489			0.402			25.2
	9	1.653	1.771	1.655			0.458			25.9
	10	0.554	0.640	0.598			0.175			27.3
	Total		7.111	6.645			2.401			
	Average		(1.422)	1.329	0.784 (calc.)	0.545 (calc.)	0.480			33.4
Final period. 3 days.	11	1.410	1.459	1.364	0.817	0.547	0.456	56.0	37.5	31.2
	12	1.805	1.896	1.772	0.970	0.802	0.571	51.2	42.3	30.1
	13	0.448	(0.431)	0.403	0.294	0.109	0.122	65.6	24.3	27.2
	14	1.329	1.499	1.401	0.866	0.535	0.373	57.8	35.7	24.9
	Total	4.992	5.286	4.940	2.947	1.993	1.522			
	Average	1.664	1.762	1.647	0.982 0.972 (calc.)	0.664 0.675 (calc.)	0.507	55.7	37.7	28.8

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Discussion of Data from Subject W, Table I.—As mentioned before the determinations of fecal nitrogen in this experiment were unsatisfactory because of the loss of volatil nitrogenous compounds in drying. That nitrogen was lost is very evident from the values of bacterial + soluble nitrogen which are in almost all cases larger than the corresponding total nitrogen. The so-called bacterial + soluble nitrogen comes from the determination of bacterial nitrogen and its significance will be clear by referring to the description of the method as given in a recent article.[1] If the acid suspension after removing the last sediment of non-bacterial substance is not treated with alcohol, but is directly transferred to Kjeldahl flasks, the nitrogen so determined is not only bacterial but includes in addition all nitrogen that is soluble in 0.2 per cent. hydrochloric acid or that has become so during the time of manipulation. This datum is spoken of as bacterial + soluble nitrogen. In later experiments it was shown that the ratio of total nitrogen to bacterial + soluble was fairly constant at 1.10 in the preliminary period and 1.07 in the following periods. Applying this factor to the values under bacterial + soluble nitrogen the values under fecal nitrogen (calc.) are obtained. Although these are not values obtained by analysis, they are more correct than those actually obtained for the reasons given. Taking either of these values, however, the average daily amount of total nitrogen excreted during the water period is only two-thirds of the average daily amount excreted during the preliminary period, and about four-fifths the average daily amount of the final period. The average daily amount in the final period is only slightly higher than that of the water period, and only three-fourths of what it was in the preliminary, showing that the good effect of the water is not immediately lost.

The question as to the kind of fecal nitrogen that was decreased in amount cannot be answered on the basis of analytical data, since the bacterial and acid-soluble nitrogen were not separated during the early part of the experiment. From later experiments in which this separation was made, a factor was calculated and found to be very uniform for different subjects throughout the various periods. On this basis 59 per cent. of the combined bacterial + soluble nitrogen is nitrogen belonging to bacterial substance. That the factor as applied does not fall far short of representing actual conditions may be gathered from the close agreement between the calculated values and those obtained by actual analysis of the stools of the final period. Applying this factor to the values for combined bacterial + soluble nitrogen the nitrogen of bacterial substance in the preliminary period was 1.279 grams per day, in the water period 0.784 gram per day, and in the final period 0.972 gram per day. These values indicate that bacterial nitrogen was de-

[1] Mattill and Hawk, *J. Exp. Med.*, 14, 433 (1911).

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creased under the influence of copious water drinking and furthermore, in common with the results found for total fecal nitrogen, this condition was not transitory but more or less permanent. The same statement may be made regarding the nitrogen soluble in 0.2 per cent. hydrochloric acid. The acid-alcohol-soluble nitrogen averaged 25.5 per cent. of the total fecal nitrogen during the preliminary period, 33.4 per cent. during the water period, and 28.8 per cent. during the final. This may mean that the digestion during the water period resulted in nitrogenous end products which are more soluble. This increased percentage of acid-alcohol-soluble nitrogen in the feces during the water period does not indicate decreased absorption, for the *absolute* amount of this form of nitrogen in the feces is *decreased* from 0.608 gram during the preliminary period to 0.480 gram in the water period and rizes only slightly above this value, 0.507 gram, during the final period, showing that absorption of the soluble end products is more complete under the influence of water. More probably, however, this form of nitrogen represents the residual portion of digestive and intestinal juices which are known to increase in amount under the influence of water ingestion, especially the gastric and pancreatic secretions and the bile. If this is so, it is a very important fact, for even though during copious water ingestion, the flow of these secretions is stimulated, and as a result of increased peristalsis the amount of cast-off cellular material in the intestin is increased, the amount of fecal nitrogen instead of being increased, as, indeed, it must be from these sources, is, on the contrary, actually *decreased*. It follows from this that the digestibility of protein material during a period of copious water-drinking was increased even beyond what the data indicate, since part of the excreted nitrogen is known to come from the larger amounts of digestive juices secreted under the stimulating influence of water.

Discussion of Data from Subject H, Table II.—The values for total fecal nitrogen, either those determined directly on dry feces or those calculated directly from the bacterial + soluble nitrogen, show that the average daily excretion of nitrogen was 1.833 g. (detd.) during the preliminary period, 1.442 g. during the water period, and 1.636 g. during the final period. It was thus much less during the water period than during either of the others, and the average daily amount after the water was less than that before it.

As with subject W, the kinds of fecal nitrogen that suffered a decrease cannot be stated on the basis of analysis. The results on applying to the value for bacterial + soluble nitrogen the factor 0.59, which was obtained from later experiments, as has been explained, show that the average bacterial nitrogen per day was decreased from 1.155 in the preliminary to 0.875 in the water period, rizing to 1.044 in the final. The average daily output as determined for the final period is 1.128, showing

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that the factor used is accurate. The same proportionate differences are to be noticed in the values for soluble nitrogen. It is evident that both bacterial and soluble nitrogen in the feces underwent a marked decrease during the period of copious water drinking.

TABLE II.—SUBJECT H.

	Number of stool.	Nitrogen distribution.						Percentage of total fecal nitrogen found in		
		Fecal nitrogen (detd.).	Fecal nitrogen (calc.	Bacterial + soluble nitrogen.	Bacterial nitrogen.	0.2 per cent. HCl soluble nitrogen.	Acid-alc.-soluble nitrogen.	Bacterial.	HCl-soluble.	Acid-alc.-soluble.
Prelim. period. 3 days.	1.....	0.636	0.743	0.675			0.208			28.0
	2.....	1.214	1.427	1.297			0.342			24.0
	3.....	2.206	2.654	2.413			0.756			28.5
	4.....	1.443	1.635	1.486			0.653			39.9
Total.....		5.499	6.459	5.871			1.959			
Average.....		1.833	2.153	1.957	1.155 (calc.)	0.802 (calc.)	0.653			30.3
Water period. 5 days.	5.....	0.514	0.537	0.502			0.280			52.1
	6.....	1.113	1.249	1.167			0.447			35.8
	7.....	0.695	0.761	0.711			0.238			31.3
	8.....	3.325	3.602	3.366			1.134			31.5
	9.....	1.563	1.788	1.671			0.655			36.6
Total.....		7.210	7.937	7.417			2.754			
Average.....		1.442	1.587	1.483	0.875 (calc.)	0.608 (calc.)	0.551			34.7
Final period. 3 days.	10.....	1.229	1.415	1.322	0.819	0.503	0.503	57.9	35.6	35.6
	11.....	0.442	0.477	0.446	0.302	0.144	0.119	63.3	30.2	24.9
	12.....	1.510	1.763	1.648	1.082	0.566	0.563	61.4	32.1	31.9
	13.....	1.726	2.028	1.895	1.180	0.715	0.671	58.2	35.3	33.1
Total.....		4.907	5.683	5.311	3.383	1.928	1.856			
Average.....		1.636	1.894	1.770	1.128	0.643	0.619	59.6	34.0	32.7
					1.044 (calc.)	0.726 (calc.)				

The percentage of acid-alcohol-soluble nitrogen rose from an average of 30.3 in the preliminary to 34.7 during the water period and fell to 32.7 in the final, while the actual amount fell from 0.653 in the preliminary to 0.551 in the water and rose to 0.619 gram per day in the final period. The actual amount of this form of nitrogen was considerably decreased under the influence of water drinking. The suggestion may be made again that the increased percentage output was probably due to the increased volume of digestive juices, the secretion of which was stimulated by the ingestion of water.

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Summary.

The findings on both subjects in this experiment show a decreased elimination of all forms of fecal nitrogen during the period in which water (1000 cc. additional) was taken with each meal. No ill effects could be seen and the beneficial effect of water was not temporary but was prolonged beyond the time during which water was taken.

Experiments on Moderate Water Drinking with Meals.

In the experiments upon protein utilization under the influence of a water ingestion of 500 cc. with each meal, the same general methods were employed. Total nitrogen determinations were made on the fresh moist material and the loss in volatil nitrogen compounds due to drying was thus avoided. A more accurate and trustworthy separation of the bacterial + soluble nitrogen was made by an efficient centrifugation of the final alcohol suspension from which the clear liquid had been pipetted off. The nitrogen of the precipitated material could more truly be called bacterial nitrogen, that of the liquid, acid-soluble nitrogen.

On the basis of the experience gained in this and similar investigations we cannot agree with certain statements made recently by Mendel and Fine[1] as to the determination of the total nitrogen content of feces. They say: "The error incident to this procedure (drying), however, did not appear to us to warrant serious attention, at least until certain details of metabolism operations, such, *e. g.*, as the accurate division of feces belonging to successive periods, reaching a higher stage of perfection." If we examin Tables I and II of the present paper it will be observed that *the values obtained by us for the combined bacterial and soluble nitrogen of fresh feces are in nearly every instance larger than the total nitrogen values obtained from the analysis of the same feces after drying.* We are firmly convinced that the ideal method of feces analysis embraces the examination of the individual stools in the *fresh* condition. This procedure, of course, entails much more labor than the less accurate practice of utilizing the dried feces, but we believe that the added accuracy richly compensates the investigator. In certain connections the individual fresh stools may be preserved for several days and an analysis made of a composit sample of the moist feces.[14b]

Throughout most of this experiment the values for bacterial nitrogen and for nitrogen in the alcohol extract of bacteria, that is the acid-soluble nitrogen, were determined along with a determination of the bacterial + soluble nitrogen, that is, the same suspension without alcohol treatment. The agreement between the last-named and the sum of the first two is very satisfactory; in almost all cases they would pass as duplicates. The fact that the alcohol used was not previously freed from pos-

[1] Mendel and Fine, *J. Biol. Chem.*, 10, 309 (1911).

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sible traces of nitrogen may account for the uniformly higher values given by the sum of the separate alcohol-soluble and bacterial determinations.

It was found from these data that the bacterial nitrogen was 59 per cent. of the combined bacterial + soluble nitrogen and this ratio was used in the preceding experiment. The ratio of total fecal nitrogen to bacterial-soluble nitrogen used in the first experiment was obtained from the values for these forms in this experiment. In both Tables III and IV this was approximately 1.10 in the earlier periods and 1.07 in the later periods.

Acid-alcohol-soluble nitrogen was determined as before, and the determination of residue nitrogen was made throughout this experiment.

The diet of subject W, who had served before, was slightly reduced from what it had been in the preceding experiment. The amounts and composition were as follows:

	Amount (per meal).	Nitrogen.
Graham crackers	125 grams	1.776 grams
Peanut butter	20 "	0.868 "
Butter	25 "	0.015 "
Milk	400 (cc.)	1.917 "
Protein		4.577
Daily protein		28.61
		85.83

The diet of subject E consisted of

Graham crackers	150 grams	2.120 grams
Peanut butter	20 "	0.868 "
Butter	25 "	0.015 "
Milk	400 (cc.)	1.917 "
Protein		4.920 "
Daily protein		30.75
		92.25

For water ingestion see preceding paper.

Discussion of Data from Subject W, Table III.—Because of the difficulty experienced in obtaining nitrogen equilibrium the preliminary period of W was divided by taking charcoal on the eighth day, but with no change in diet. On the 13th day W's nitrogen balance was as follows:

Nitrogen in feces	1.360
Nitrogen in urine	12.361
Nitrogen in excreta	13.721
Nitrogen in food	13.731
	+0.010

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The influence of a restricted amount of water and the latent period after which its effects appeared, as explained in the previous paper, are to be noted in the protein utilization as they were in the fat utilization. The average daily fecal nitrogen excretion during the first part of the preliminary period rizes from 1.275 to 1.360 in the second part, bacterial + soluble nitrogen from 1.142 to 1.233, acid-alcohol-soluble from 0.284 to 0.320, and residue nitrogen from 0.148 to 0.154. A comparison of the nitrogen data of this preliminary period with the nitrogen data of the preliminary period of the first experiment shows the average daily total fecal nitrogen output to be 2.385 in the first as against 1.275 in the second; bacterial + soluble nitrogen 2.168 in the first as against 1.142 in the second; acid-alcohol-soluble 0.608 as against 0.284. The average percentage utilization of protein in the first experiment was 86.3 per cent. as against 90.7 per cent. in the second. These data showing so pronounced an improvement in the digestion and utilization of protein are on an individual living on the same kind of diet, but separated by a period of three months in which water drinking with ordinary meals was practised.

With the fourteenth day 500 cc. of water were added to the diet of of each meal and this was continued for ten days. A five-day period followed in which the original conditions prevailed.

By referring to Table III it will be seen at once that the nitrogen of the various periods presents no striking differences.

The values for total, bacterial and other forms show fluctuations which are too small to admit of conclusions. The largest proportionate variation is seen in the residue nitrogen. This, as was explained, was obtained from the solid material that was sedimented in the procedure for bacterial nitrogen. Its percentage of the total nitrogen, 11.3, in the preliminary period, fell to 9.5 in the water period, and still lower, to 8.2 in the final period. If these small differences are significant, they point to a condition of better digestion.

Discussion of Data from Subject E, Table IV.—On the diet given, the nitrogen balance of Subject E at the end of the sixth day was as follows:

Nitrogen in feces	1.926
Nitrogen in urine	13.320
Nitrogen in excreta	15.246
Nitrogen in food	14.761
	—0.485

An examination of the data in Table IV again reveals no striking differences in the nitrogen values from one period to another. The variations in average daily amounts of nitrogen in its various forms are, as in the case of W, too small to be significant, with the possible exception of the

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TABLE III.—SUBJECT W.

	Number of stool.	Nitrogen partition. Total fecal nitrogen.	Bacterial + soluble nitrogen.	Bacterial soluble separate.	Bacterial nitrogen.	0.2 per cent. HCl soluble nitrogen.	Acid-alc.-soluble nitrogen.	Residue nitrogen.	Percentage of total fecal nitrogen found in: Bacterial + soluble nitrogen.	Bacterial.	0.2 per cent. HCl soluble.	Acid-alc.-soluble.	Residue.
Prel. per. I. 7 days.	1	2.152	1.906				0.460	0.323	88.6			21.4	15.0
	2	0.618	0.556				0.143	0.076	90.0			23.2	12.2
	3	0.878	0.789				0.213	0.100	89.9			24.3	11.4
	4	1.070	0.990				0.234	0.109	92.5			21.9	10.2
	5	3.075	2.760				0.684	0.269	89.8			22.3	8.8
	6	1.131	0.993				0.255	0.159	87.8			22.6	14.0
Total		8.924	7.994				1.990	1.035					
Average		1.275	1.142				0.284	0.148	89.6			22.3	11.6
Prel. per. II. 6 days.	7	0.845	0.790	0.816	0.483	0.336	0.190	0.071	93.6	57.2	39.5	22.5	8.4
	8	1.265	1.208	1.199	0.693	0.506	0.277	0.127	95.5	54.8	40.0	21.9	10.0
	9	1.491	1.324	1.388	0.791	0.597	0.362	0.132	88.8	53.0	40.1	24.3	8.9
	10	2.213	2.008	2.057	1.107	0.949	0.544	0.271	90.7	50.0	42.9	24.6	12.3
	11	0.673	0.574	0.549	0.287	0.262	0.161	0.109	85.3	42.6	39.0	23.9	16.1
	12	1.254	1.136	1.084	0.590	0.494	0.298	0.169	90.6	47.0	39.4	23.8	13.5
	13	0.418	0.355	0.358	0.194	0.163	0.088	0.044	85.1	46.6	39.1	21.8	10.5
Total		8.157	7.396	7.450	4.144	3.306	1.920	0.922					
Average		1.360	1.233	1.242	0.691	0.551	0.320	0.154	90.7	50.8	40.5	23.5	11.3

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Water period 10 days. 14	0.388	0.352	0.368	0.200	0.168	0.103	0.028	90.6	51.4	43.3	26.5	7.2
15	2.044	1.959	1.867	0.984	0.884	0.530	0.207	95.8	48.1	43.2	25.9	10.1
16	1.029	0.990	0.986	0.563	0.424	0.249	0.083	96.3	54.7	41.2	24.2	8.0
17	2.044	1.929	1.929	1.087	0.841	0.521	lost	94.4	53.2	41.2	25.5	....
18	0.899	0.790	0.831	0.440	0.390	0.215	0.123	87.8	49.0	43.4	24.0	14.0
19	1.616	1.510	1.495	0.873	0.621	0.404	0.163	93.4	54.0	38.4	25.0	10.1
20	0.377	0.337	0.345	0.198	0.147	0.087	0.042	89.3	52.5	39.1	23.0	11.1
21	2.355	2.249	2.254	1.298	0.957	0.583	0.195	95.5	55.1	40.6	24.8	8.3
22	1.672	1.533	1.549	0.881	0.668	0.409	0.172	91.7	52.7	40.0	24.5	10.3
23	1.918	1.751	1.813	0.996	0.817	0.498	0.211	91.3	51.9	42.6	26.0	11.0
Total	14.343	13.400	13.437	7.520	5.917	3.599	1.224					
Average	1.434	1.340	1.344	0.752	0.592	0.360	0.136	93.4	52.4	41.3	25.1	9.5
Final period 5 days. 24	0.775	0.730	0.724	0.416	0.307	0.184	0.062	94.2	53.7	39.6	23.8	8.0
25	1.497	1.383	1.391	0.823	0.568	0.355	0.099	92.4	55.0	38.0	23.7	6.6
26	0.758	0.694	(0.694)	0.461	0.233	0.195	0.079	91.6	60.9	30.3	25.7	10.5
27	1.845	1.738	1.955	1.160	0.795	0.488	0.163	94.2	62.9	43.1	26.5	8.8
28	1.238	1.153	1.201	0.758	0.444	0.292	0.100	93.1	61.2	35.8	23.6	8.1
29	0.875	0.830	0.872	0.539	0.333	0.207	0.070	94.8	61.6	38.1	23.6	8.0
Total	6.988	6.528	6.837	4.157	2.680	1.721	0.573					
Average	1.398	1.306	1.368	0.832	0.536	0.344	0.115	93.4	59.5	38.4	24.6	8.2

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TABLE IV.—SUBJECT E.

		Nitrogen distribution.							Percentage of total fecal nitrogen found in				
		Total fecal nitrogen.	Bacterial +soluble nitrogen.	Bacterial soluble separate.	Bacterial nitrogen.	0.2 per cent. HCl soluble nitrogen.	Acid-alc.-soluble nitrogen.	Residue nitrogen.	Bacterial +soluble.	Bacterial.	0.2 per cent. HCl soluble.	Acid-alc.-soluble.	Residue.
Prel. period. 7 days.	1.....	1.141	0.945				0.236	0.159	82.8			20.7	13.9
	2.....	0.461	0.457				0.106	0.056	99.1			23.0	12.1
	3.....	2.420	2.251				0.530	0.235	93.0			21.9	9.7
	4.....	2.867	2.591				0.679	0.312	90.4			23.7	10.9
	5.....	1.219	1.104				0.262	0.130	90.6			21.5	10.7
	6.....	2.846	2.587				0.654	0.328	90.9			23.0	11.9
	7.....	1.744	1.581				0.366	0.206	90.6			21.0	11.8
	8.....	0.784	0.731				0.176	0.072	93.3			22.5	9.2
Total.....		13.481	12.247				3.010	1.497					
Average.....		1.926	1.750				0.430	0.214	90.9			22.3	11.1

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Water period. 10 days. 9.....	1.048	0.923	0.921	0.536	0.386	0.233	0.138	88.0	51.1	36.8	22.2	13.2
10.....	1.837	1.713	1.723	1.085	0.638	0.380	0.194	93.2	59.1	34.7	20.7	10.6
11.....	1.158	1.087	1.091	0.685	0.406	0.241	0.072	93.9	59.2	35.1	20.8	6.3
12.....	2.577	2.398	2.405	1.372	1.033	0.571	0.214	93.0	53.3	40.1	22.2	8.3
13.....	3.133	2.678	2.700	1.443	1.257	0.713	0.376	85.5	46.1	40.1	22.8	12.0
14.....	1.896	1.706	1.767	1.019	0.748	0.419	0.192	90.0	53.8	39.5	22.1	10.1
15.....	2.389	2.059	2.165	1.083	1.081	0.589	0.242	86.2	45.4	45.3	24.7	10.1
16.....	1.144	1.015	1.032	0.523	0.509	0.264	0.140	88.7	45.7	44.5	23.1	12.3
17.....	0.811	0.806	0.787	0.425	0.362	0.207	0.102	99.4	52.4	44.7	25.5	12.6
18.....	2.567	2.377	2.353	1.343	1.010	0.630	0.232	92.6	52.3	39.3	24.5	9.0
19.....	0.818	0.790	0.808	0.445	0.363	0.205	0.075	96.5	54.4	44.4	25.1	9.2
Total.....	19.378	17.551	17.752	9.958	7.794	4.452	1.978					
Average.....	1.938	1.755	1.775	0.996	0.779	0.445	0.198	90.6	51.4	40.2	23.0	10.2
Final period. 4 days. 20.....	0.943	0.829	0.828	0.425	0.403	0.213	0.146	87.9	45.1	42.7	22.5	15.4
21.....	1.855	1.675	1.703	1.015	0.688	0.429	0.196	90.3	54.7	37.1	23.1	10.6
22.....	2.045	1.861	1.864	1.068	0.796	0.446	0.199	91.0	52.2	38.9	21.8	9.8
23.....	2.251	2.086	2.158	1.243	0.915	0.556	0.230	92.7	55.2	40.6	24.7	10.2
24.....	0.538	0.493	0.502	0.195	0.308	0.126	0.059	91.7	36.2	57.2	23.4	10.9
Total.....	7.631	6.944	7.055	3.946	3.109	1.769	0.830					
Average.....	1.908	1.736	1.764	0.987	0.777	0.442	0.207	91.0	51.7	40.7	23.2	10.9

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values for the residue nitrogen. The percentage of the total nitrogen found in this form during the preliminary period, 11.1, fell to 10.2 in the water period and rose to 10.9 in the final. Similar variations, and in the same direction, were noted with W. Attention may be called again to the satisfactory agreement of the values for bacterial + soluble nitrogen with the values of the sum of these two determined separately, which thus furnishes a valuable check on the determinations.

The protein data on Subjects W and E during this experiment on moderate water drinking with meals do not justify the drawing of any but negative conclusions; they do not show that the use of water was attended by any undesirable results. The data obtained on the utilization of carbohydrate and fat during this period, which are presented in the following and preceding papers, show that where analytical methods are sufficiently exact to give significant results the effect of moderate water drinking is in the same direction as that of copious water drinking, though much less marked.

Copious Water Ingestion by an Individual Accustomed to Taking Considerable Water with Meals.

Following the preceding experiment, a period of six days formed the preliminary period for this experiment, the subject of which was E. The diet was the same as before and at the beginning of the 5-day water period the nitrogen balance was as follows:

Nitrogen in feces	1.957
Nitrogen in urine	12.775
Nitrogen in excreta	14.732
Nitrogen in food	14.761
	+0.029

Discussion of Data on Subject E, Table V.—Although both carbohydrate and fat data (discussed in other places) show differences that signify an increased utilization of these foodstuffs during the ingestion of one and one-third liters of water additional with each meal, a comparison of the data on the excretion of nitrogen in its various forms during the three periods of this experiment allows no positive conclusions to be drawn. The differences are too small to be significant. A negative conclusion, however, is entirely justifiable, when it is seen that the absorption of over four liters of water during the day, and most of this taken during the meals, had no untoward effect upon the digestion and absorption of the food. The probable reason for the fact that no change in the direction of better digestion could be noticed is that Subject E habitually took considerable amounts of water with his meals, and the experimental conditions were thus little different from the usual régime.

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TABLE V.—SUBJECT E.

		Nitrogen distribution.							Percentages of total fecal nitrogen found in				
		Total fecal nitrogen.	Bacterial + soluble nitrogen.	Bacterial soluble separate.	Bacterial nitrogen.	0.2 per cent. HCl soluble nitrogen.	Acid-alc.-soluble nitrogen.	Residue nitrogen.	Bacterial + soluble.	Bacterial.	0.2 per cent. HCl soluble.	Acid-alc.-soluble.	Residue.
Prel. period. 6 days.	1	0.572	0.517	0.521	0.307	0.214	0.131	0.067	90.4	53.7	37.4	22.9	11.7
	2	1.116	1.051	1.094	0.692	0.402	0.273	0.073	94.2	62.1	36.0	24.5	6.5
	3	3.036	2.821	2.898	1.715	1.183	0.706	0.233	92.9	56.5	39.0	23.2	7.7
	4	1.940	1.813	1.836	1.088	0.748	0.451	0.176	93.5	56.1	38.6	23.3	9.1
	5	2.104	2.003	2.066	1.205	0.861	0.489	0.174	95.2	57.3	40.9	23.2	8.3
	6	2.383	2.175	2.225	1.264	0.961	0.521	0.252	91.3	53.1	40.3	21.9	10.6
	7	0.591	0.553	0.570	0.364	0.206	(0.080)	0.042	93.7	61.5	34.9	(13.5)	7.1
Total		11.741	10.933	11.210	6.635	4.575	2.650	1.016					
Average		1.957	1.822	1.868	1.106	0.763	0.457	0.169	93.1	56.5	39.0	(23.4)	8.7
Water period. 5 days.	8	1.119	1.026	1.069	0.640	0.424	0.250	0.115	91.7	57.1	37.9	22.4	10.3
	9	0.627	0.590	0.606	0.365	0.241	0.143	0.050	94.1	58.2	38.5	22.8	8.0
	10	3.633	3.429	3.512	2.040	1.472	0.756	0.292	94.4	56.2	40.5	20.8	8.0
	11	1.216	1.103	1.130	0.659	0.471	0.285	0.103	90.7	54.2	38.8	23.4	8.5
	12	2.250	2.095	2.178	1.081	1.097	0.570	0.225	93.1	48.1	48.7	25.3	10.0
	13	0.994	0.885	0.916	0.528	0.389	0.213	0.077	93.8	55.8	41.2	22.6	8.2
Total		9.788	9.128	9.411	5.312	4.094	2.216	0.861					
Average		1.958	1.826	1.882	1.062	0.819	0.443	0.172	93.3	54.3	41.8	22.6	8.8
Final period. 3 days.	14	1.790	1.658	1.712	1.042	0.670	0.389	0.189	92.6	58.2	37.4	21.7	10.6
	15	1.336	1.241	1.283	0.767	0.516	0.304	0.111	92.9	57.4	38.6	22.8	8.3
	16	2.800	2.561	2.664	1.555	1.109	0.607	0.250	91.5	55.5	39.6	21.7	8.9
	17	0.340	0.303	0.300	0.159	0.141	0.092	0.040	89.3	47.0	41.4	27.0	11.8
Total		6.265	5.763	5.958	3.523	2.435	1.392	0.590					
Average		2.088	1.921	1.986	1.174	0.812	0.464	0.197	92.0	56.2	38.9	22.2	9.4

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General Discussion.

The general conclusion from all these findings is that during water ingestion with meals there is a better digestion and a more complete utilization of the protein food and that this effect is much less marked with a small water ingestion than with a large one. It is also more or less permanent, with the result that in an individual accustomed to taking considerable water with meals the effects of decreasing or increasing the volume ingested are not immediately obvious.

There is one objection to the conclusion that this is caused by water drinking. It has frequently been observed in experiments on men that the prolonged administration of a given diet causes the enzyme content of the digestive juices so to change as to be best adapted to digesting the food. It might be argued, therefore, that although the food was as well digested during the latter part of these experiments as in the beginning, this was a result of adaptation which counteracted the undesirable effects of water drinking. A comparison of the data of the final periods with those of the water periods is sufficient to show that the withdrawal of water was accompanied by a pronounced change in favor of the water drinking, or by no appreciable change in digestibility and utilization.

Any supposed effect of adaptation is also counterbalanced by the effect of loss of appetite due to the monotony of the diet. London and Pevsner[15] found that in dogs the stomach contents were more rapidly passed on to the duodenum when the factor of appetite was present than when it was absent. They conclude that the larger amount of secretion, that is, the appetite juice, was the cause. If there is any increased efficiency in "appetite" juice over the ordinary secretion in man then the digestive power of all the juices is at least not increased by the factor of appetite after partaking of over one hundred meals that were absolutely uniform in the kind and quantity of food they contained.

Evidence has been adduced in another place to show that the action of water is not such as to cause undigested food particles to be washed through the pylorus prematurely, and thereby place a more than proportionate burden upon the lower digestive tract. That a premature opening of the pylorus, resulting in a shortening of gastric digestion, is uneconomical, has been shown by Cohnheim.[16] The importance of the stomach in protein digestion is not clear despite extensive experimentation bestowed upon the subject.

London and Polovzova[17, 18] found that with but few exceptions proteins are not absorbed in the stomach, but that with few exceptions most proteins are made soluble in the stomach to about 78 per cent., the ratio between proteoses, peptones and residual substances being 59.3, 32.9, 7.8. The soluble products of gastric digestion are quickly attacked by the in-

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testinal juices. Examination of stomach contents[19] reveals the fact that peptones, peptides and amino acids may be absorbed; while it is shown that the enzymes of the stomach have the ability completely to hydrolyze proteins to these end-products, yet it is also shown that the length of time which pepsin requires to bring this about is far in excess of the time in which protein remains in the stomach.

The importance of the stomach in protein assimilation has been emphasized recently by Carrel, Meyer and Levene,[20] who showed that after removal of the larger part of the small intestin, although the absorption of ingested protein is diminished, the rate of assimilation and retention of the absorbed protein follows the same course as in normal animals. They conclude that the stomach and not the intestin is the most important organ for protein assimilation. London and Dmitriev[21] showed that the removal of the small intestin in a dog results in the death of the animal in about five weeks. Ordinarily, if as much as seven-eighths of the small intestin is removed, carbohydrate and especially protein assimilation rapidly return to normal but not so with the assimilation of fat. Somewhat similar results have been obtained by Underhill.[22] After resection of 80 per cent. of the small intestin Axhausen[23] found that the absorption of protein as well as of fat was very much lower than normal. Results obtained after experimental removal of various portions of the alimentary tract are always subjected to this correction that the different organs may change their function and character in the direction of compensation. Thus, after gastrectomy in dogs, Carrel, Meyer and Levene[24] observed a high nitrogen retention which disappeared in ten to twelve weeks after the operation. The explanation suggested is that the pancreatic and intestinal secretions that are minimal immediately after gastrectomy return to normal at a later period and protein is again fully digested before absorption. They also note a hypertrophy of the upper end of the duodenum after gastrectomy.

Since the presence of water along with food in the stomach is hardly of long enough duration to affect either the food or the mucous membrane, the changes for the better digestion and utilization of the protein material that have been observed must take place principally in the intestin. Some experimental work has been done on the absorption of proteins by living membranes. Zunz[25] in experiments on dogs upon protein digestion and absorption in the stomach and small intestin *in situ* has shown that the osmotic pressure of the solutions of protein introduced scarcely changes in the stomach when this is tied off, but in the small intestin it tends toward that of the blood and usually becomes lower than this. Surface tension is lower than that of the blood in both the stomach and intestin. With low proteose content the surface tension decreases in both regions. In the intestin, Zunz concludes, the digestive

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processes tend to bring the concentration, osmotic pressure and surface tension of the contents to the optimum for absorption. The organism itself seems to strive to secure a dilution of the products of digestion such that they can be most readily and completely absorbed.

The phenomena of absorption still lack a unifying physical explanation; in fact, each investigation seems to disclose new and unknown factors. Filtration, osmosis, the selective action of membranes and the nature and behavior of colloids are some of the important factors, upon an understanding of which the solution of the many problems depends.

Conclusions.

Without attempting to suggest any further explanations than those given at the end of the preceding paper, it may be said that the ingestion of large amounts (1000 cc.) of water with meals caused the protein constituents of the food to be more completely utilized, as shown by a decrease in all forms of nitrogen in the feces, including bacterial, 0.2 per cent. hydrochloric-acid-soluble, acid-alcoholic extractive, and residue nitrogen.

When 500 cc. of water were taken with meals no significant changes in protein utilization could be observed, as there were in fat and carbohydrate; the protein data do, however, admit of the negative conclusion, that absolutely no undesirable effects were to be observed as a result of the ingestion of 500 cc. of water with the meals. Even when over four liters of water were taken daily, with the meals, there was no indication of untoward effects as a result.

As before, the beneficial results of water ingestion with meals were not transitory, but were more or less permanent, extending beyond the time of the experimental period.

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STUDIES ON WATER DRINKING: X. FECAL OUTPUT AND ITS CARBOHYDRATE CONTENT UNDER THE INFLUENCE OF COPIOUS AND MODERATE WATER DRINKING WITH MEALS.

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Introduction.

It has been said that the amount of feces, as well as its nitrogen content, depends entirely upon the cellulose content of the food materials, the first being the result of the inability of the organism to digest cellulose, the second being due to the increased desquamation of intestinal epithelium as a result of heightened peristalsis and to an accompanying increase in the amount of digestive fluids secreted.

Aside from possible traces of the less common complex carbohydrates, the only carbohydrates ever present in normal feces under ordinary conditions are cellulose and starch. It has been shown by Lusk[1] that the decomposition of cellulose does not result in the formation of glucose, and its nutritive value is probably in the fatty acids formed from it. In a study of the digestibility of carbohydrate, therefore, a consideration of the possible digestion of cellulose is unnecessary.

The source of starch in the feces is ingested vegetable food, the cellulose envelopes of which, as a result of insufficient disintegration, have not become accessible to the action of the digestive juices. The manner of preparing the food has much to do with the extent of this disintegration; the efficiency of the mastication also plays a part, and the activity of the digestive juices and the extent of the churning to which the food is subjected in the intestin also have an influence. All other conditions remaining the same, the amount of carbohydrate found in the feces should furnish some indication as to the digestibility of carbohydrate in the organism, as well as to the extent of cellular disintegration by which it has become available. In the series of observations reported in the preceding papers on the utilization of protein and fat under the conditions of water drinking with meals attention was also paid to the comparative

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amounts of fecal dry matter and moisture, and to the utilization of carbohydrate, although the diet consisted of almost completely available food and contained little cellulose.

The early experiment of Ruzicka[2] previously referred to included certain data upon total fecal excretion. During the first 2-day period (no water with meals) the total fecal dry matter was 46.2 grams against 42.0 grams in the second 2-day period when water was taken with meals. The total dry matter ingested during the first (no water) period was 783.3 grams, while the dry matter ingested in the second period was 842.5 grams. The carbohydrate intake and excretion (obtained by difference) for the two periods were as follows:

	First period (no water). Grams.	Second period (water). Grams.
Ingesta	357.4	384.4
Excreta	6.9	6.3

It is thus seen that the ingestion both of total dry matter and of carbohydrate was larger in the water period than in the period when no water was taken with the meals, while the excretion both of total dry matter and of carbohydrate was smaller when water was taken with meals than when none was taken. The diet was one of bread and meat, and analyses are given which show that the feces were of relatively the same composition in both periods; 100 grams of the dry substance yielding 14.9 and 15.0 grams, respectively, of carbohydrate.

In the investigation of Fowler and Hawk[3] referred to in the previous paper the elimination of fecal dry matter and moisture during the period of water ingestion with meals was much less than during either the fore or after period. No data were obtained on carbohydrate utilization.

Methods.—In the paper on fat utilization will be found a description of the method of collecting and preparing the sample. *Moisture.* Moisture was determined, during one experiment, in porcelain crucibles, during a second in lead caps. The latter method is much more satisfactory. The samples were first air-dried for two or three days, and then in an oven at 102°, for two or three days.

Carbohydrate.—Carbohydrate was determined by a modification of the method of Strasburger.[4] The procedure was as follows: Five to 10 grams of feces were weighed out into a 200 cc. Erlenmeyer flask, and 5–7 grams of bone-black were added along with 100 cc. of 5 per cent. hydrochloric acid. This mixture was boiled for one and one-half to two hours under a reflux condenser, allowed to cool, made alkaline with sodium hydroxide to precipitate calcium salts and filtered with suction. Ordinarily this took considerable time. The filtrate was clear and varied in color from a dark straw to entire absence of color. This solution was approximately neutralized and its reducing power was determined in an

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aliquot portion by the method of Benedict.[5] The procedure of Strasburger involves the determination of sugar by the copper thiocyanate method of Volhard-Pflüger, and the time and labor required in this method are considerably greater than for the method used in these experiments. In most cases, also, satisfactory duplicates were obtained. The solutions as prepared for the determination could never be allowed to stand any length of time with neutral or slightly alkaline reaction as the development of molds brought about decompositions and destruction of sugar. When they were left standing they were always acidified.

Experiments on Copious Water Drinking with Meals.

The routine of the experiment on Subjects H and W has been described in a preceding paper. The diet of both men contained carbohydrate as follows:

	Amount (per meal).	Carbohydrate.
Graham crackers	150.0 grams	108.8 grams
Peanut butter	20.0	3.2
Milk	450.0 (cc.)	25.7
Butter (carbohydrate negligible)	25.0	
	Total,	137.7

For water ingestion see paper on fat utilization.

Discussion of Data from Subject W, Table I.—The average amount of

TABLE I.—SUBJECT W.

	Number of stool.	Weight. Grams.	Per cent. dry matter.	Amount dry matter. Grams.	Amount moisture. Grams.	Carbohydrate. Grams.
Prel. period. 3 days	1	147.0	27.33	40.2	106.8	1.955
	2	182.5	25.86	47.2	135.3	2.71
	3	66.0	27.21	18.0	48.0	1.12
	4	138.0	23.67	32.7	105.3	1.78
Total		533.5	...	138.1	395.4	7.565
Average (per day)		177.8	25.9	46.0	131.8	2.52
Water period. 5 days	5	214.0	13.17	28.2	185.8	2.09
	6	25.2	23.24	5.9	19.3	0.26
	7	94.0	27.34	25.7	68.3	1.51
	8	102.8	28.85	29.7	73.1	1.56
	9	121.5	26.05	31.6	89.9	1.87
	10	39.0	29.83	11.6	27.4	0.47
Total		596.5	...	132.7	463.8	7.76
Average (per day)		119.3	22.2	26.5	92.8	1.55
Final period. 3 days	11	104.5	25.48	26.6	77.9	1.40
	12	134.0	25.83	34.6	99.4	2.09
	13	26.9	31.85	8.6	18.3	0.38
	14	98.0	26.10	25.6	72.4	1.55
Total		363.4	...	95.4	268.0	5.42
Average (per day)		121.1	26.3	31.8	89.3	1.81

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feces passed per day during the preliminary period was 177.8 grams, during the water period 119.3 grams, and during the final period 121.1 grams. A similar variation is observed in the fecal dry matter which decreases from 46 grams per day in the preliminary to 26.5 grams in the water period and again rizes in the final to 31.8 grams. The average daily amount of water in the feces of the preliminary period was 131.8 grams, in the water period 92.8 grams and in the final period 89.3 grams. Notwithstanding the large amount of water passed into the intestin during the water period, there was less in the feces during that time than before; the amount of water excreted in the feces in the final period was slightly less than the amount in the water period. The total amount of feces and of dry matter for the final period were only slightly higher than those of the water period and not nearly as high as those of the preliminary.

Digestion and Absorption of Carbohydrate.—The average daily excretion of carbohydrate during the preliminary period was 2.52 grams, during the water period 1.55 grams, and during the final period 1.81 grams. It appears that the effect of the large amount of water was to secure a better digestion and more complete utilization of the ingested carbohydrate, and the influence of the water extended beyond the time in which it was used.

The amount of carbohydrate in Stool No. 5, the first of the water period is 2.09 grams, the largest amount during any day of the period. This is the more striking since the entire stool contained only 28.2 grams solid matter, of which 5.8 grams were fat. The total nitrogen was also above the average, and the bacterial and extractive or acid-alcohol-soluble portions were unusually low. All of these facts indicate incomplete digestion of the food. Stool No. 5 was passed immediately after breakfast on the morning of the second day of water. Before breakfast Stool No. 4 had been passed; this contained none of the charcoal that had been taken before breakfast on the morning of the day before, the first day of the water. Charcoal was found in No. 5. W records a feeling of pressure on the first day of water as well as on the second, but on the second it seemed to increase. Stool No. 5 gives evidence from its high content of water and of foodstuffs that it was forced out before the time necessary for satisfactory digestion and absorption. Notwithstanding that this, the first stool of the water period contained undigested protein, fat and carbohydrate, nevertheless an examination of the data shows that the average daily output of those substances was markedly lowered under the influence of water ingestion.

Discussion of Data from Subject H, Table II.—The average daily amount of feces passed during the water period was less than that in either preliminary or final periods. The average amount in the period after the

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water is less than that in the period before the water. The average daily dry matter suffered a similar drop during the water period. The amount of water in the feces during the water period was also less than during the

TABLE II.—SUBJECT H.

	Number of stool.	Weight. Grams.	Per cent. dry matter.	Amount dry matter. Grams.	Amount moisture. Grams.	Carbohydrate. Grams.
Prel. period. 3 days	1	42.5	29.42	12.5	30.0	0.57
	2	87.0	26.54	23.1	63.9	1.20
	3	158.0	26.57	42.0	116.0	2.37
	4	104.0	26.21	27.3	76.7	1.80
Total		391.5	...	104.9	286.6	5.94
Average (per day)		130.5	26.8	35.0	95.5	1.98
Water period. 5 days	5	54.0	17.71	9.6	44.4	0.66
	6	81.7	27.95	22.8	58.9	1.45
	7	43.0	31.68	13.6	29.4	0.82
	8	269.5	24.33	65.6	203.9	3.89
	9	141.0	22.00	31.0	110.0	1.87
Total		589.2	...	142.6	446.6	8.69
Average (per day)		117.8	24.2	28.5	89.3	1.74
Final period. 3 days	10	101.0	23.90	24.1	76.9	1.06
	11	25.5	33.40	8.5	17.0	0.37
	12	112.0	27.90	31.3	80.7	1.71
	13	141.5	25.92	36.7	104.8	1.92
Total		380.0	...	100.6	279.4	5.06
Average (per day)		126.7	26.2	33.5	93.1	1.69

preliminary or final periods showing that even with the large amounts of water sent into the intestin the amount absorbed was actually more than the excess administered.

Carbohydrate.—The data from the carbohydrate determinations are not as striking as those from Subject W but the variations are in the same direction. The average daily excretion during the preliminary period, 1.98 grams, fell to 1.74 grams during the water period, and was still less, 1.69 grams per day, in the final period.

Summary.—The findings obtained in this experiment show that during the period when large amounts of water were taken with meals the total amounts of feces, of fecal dry matter and of fecal moisture were less than without the unusual amounts of water, and that a more or less permanently better utilization of carbohydrate accompanied the water drinking.

Experiments on Moderate Water Drinking.

Before considering the data obtained in the experiment on moderate water drinking a word of explanation should be given regarding Sub-

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ject E. During the preceding year while he was serving as subject on another metabolism experiment and was on a uniform diet a pronounced intestinal fermentation made itself evident by a stool of high moisture content. Although he was subject to a condition of this kind even on an ordinary mixed diet he made no mention of this and was therefore accepted for the present metabolism study. The condition was one apparently peculiar to the organism and was not dependent upon such external conditions as could easily be determined and controlled. Subject W had served in the preceding experiment.

The diets of the two men were alike in composition but differed slightly in quantity.

SUBJECTS W.

	Amount (per meal).	Carbohydrate.
Graham crackers	125 grams	90.6 grams
Peanut butter	20	3.2
Milk	400 (cc.)	22.8
Butter (carbohydrate negligible)	25	
	Total,	116.6

SUBJECT E.

	Amount.	Carbohydrate.
Graham crackers	150 grams	108.8 grams
Peanut butter	20	3.2
Milk	400 (cc.)	22.8
Butter (carbohydrate negligible)	25	
	Total,	134.8

For water ingestion see paper on fat utilization.

In addition to the weights of feces, dry matter and moisture, the values for the daily excretion of dry bacteria are also given; the values have been calculated from the bacterial nitrogen values on the basis of a nitrogen content of dry bacteria equal to 10.96 per cent.; this is more fully explained by us in a recent paper on the method for determining bacterial nitrogen.*

Discussion of Data from Subject W, Table III.—The separation of the preliminary period of low water ingestion into two parts showed a condition for carbohydrate and for total fecal output similar to that noted for fat and protein. The average amount of feces passed per day during the first part of this period was 89.0 grams, as against 104.6 grams in the second. The average daily dry matter content during the first part of this period was 23.9 grams as against 27.3 grams during the second part. The differences are small but not inconsiderable. Carbohydrate also shows an increase from 2.15 grams per day in the first part to 2.31 grams in the second. Comparing this preliminary period with that of the first experiment, the average daily amount of feces in the first experiment was

* Mattill and Hawk: *J. Exp. Med.*, 14, 433 (1911).

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TABLE III.—SUBJECT W.

	Number of stool.	Weight. Grams.	Per cent. dry matter	Amount dry matter. Grams.	Amount moisture. Grams.	Bacterial dry substance. Grams.	Carbohydrate. Grams.
Prel. period I. 7 days	1.....	155.5	25.94	40.3	115.2	...	3.16
	2.....	39.2	31.57	12.4	26.8	...	1.14
	3.....	63.7	27.78	17.7	46.0	...	1.92
	4.....	72.0	28.92	20.8	51.2	...	1.89
	5.....	201.8	27.04	54.6	147.2	...	5.22
	6.....	90.9	23.50	21.4	69.5	...	1.74
Total.....		623.1	...	167.2	455.9	...	15.07
Average (per day).....		89.0	26.85	23.9	65.1	...	2.15
Prel. period II. 6 days	7.....	62.8	25.61	16.1	46.7	4.40	1.52
	8.....	98.8	26.72	26.4	72.4	6.32	2.08
	9.....	109.8	27.50	30.2	79.6	7.21	3.05
	10.....	185.8	24.10	44.8	141.0	10.10	3.58
	11.....	41.8	31.23	13.1	28.7	2.62	1.03
	12.....	104.9	24.28	25.5	79.4	5.38	2.15
	13.....	24.0	32.87	7.9	16.1	1.78	0.45
Total.....		627.9	...	164.0	463.9	37.80	13.86
Average (per day).....		104.6	26.10	27.3	77.3	6.30	2.31
Water period. 10 days	14.....	31.6	23.90	7.6	24.0	1.82	0.25
	15.....	147.5	27.52	40.6	106.9	8.98	2.25
	16.....	75.4	26.20	19.8	55.6	5.13	1.20
	17.....	144.8	27.45	39.8	105.0	9.92	2.60
	18.....	63.9	26.84	17.2	46.7	4.02	1.37
	19.....	115.5	27.10	31.3	84.2	7.97	2.51
	20.....	26.0	27.49	7.2	18.8	1.81	0.56
	21.....	169.0	26.52	44.8	124.2	11.84	4.60
	22.....	127.0	24.35	30.9	96.1	8.04	2.93
	23.....	152.7	23.26	35.5	117.2	9.08	3.54
Total.....		1053.4	...	274.7	778.7	68.60	21.81
Average (per day).....		105.3	26.12	27.5	77.8	6.86	2.18
Final period. 5 days	24.....	60.0	24.67	14.8	45.2	3.80	1.34
	25.....	119.6	23.38	28.0	91.6	7.51	2.41
	26.....	51.1	27.50	14.1	37.0	4.21	1.10
	27.....	142.7	25.05	35.8	106.9	10.59	2.27
	28.....	81.4	27.96	22.8	58.6	6.91	1.82
	29.....	53.4	30.61	16.4	37.0	4.91	1.39
Total.....		508.2	...	131.9	376.3	37.92	10.33
Average (per day).....		101.6	25.90	26.3	75.3	7.59	2.07

177.8 grams as against 89.0 in the second; dry matter 46.0 grams in the first as against 23.9 in the second; carbohydrate 2.52 grams in the first as against 2.15 in the second.

Carbohydrate.—An examination of the data upon carbohydrate excre-

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tion during the ten-day water period reveals differences that are small but nevertheless in the same direction as noted in the experiment on copious water drinking. The daily average excretion in the preliminary period 2.31 grams, fell to 2.18 grams in the water period, and was still lower, to 2.07 grams, in the final period.

Discussion of Data from Subject E, Table IV.—The findings upon the fecal output of Subject E during the three periods of this experiment show variations so small that they admit of no conclusions.

TABLE IV.—SUBJECT E.

	Number of stool.	Weight. Grams.	Per cent. dry matter.	Amount dry matter. Grams.	Amount moisture. Grams.	Bacterial dry substance. Grams.	Carbohydrate. Grams.
Prel. period. 7 days	1. . . .	88.4	20.81	18.4	70.0	...	2.48
	2. . . .	30.2	26.56	8.0	22.2	...	1.18
	3. . . .	179.2	23.01	41.2	138.0	...	4.98
	4. . . .	193.9	24.67	47.8	146.1	...	7.21
	5. . . .	76.9	26.17	20.1	56.8	..	2.37
	6. . . .	207.7	22.78	47.3	160.4	...	5.31
	7. . . .	124.6	22.30	27.8	96.8	...	3.49
	8. . . .	44.0	29.42	12.9	31.1	...	1.38
Total.		944.9	...	223.7	721.2	...	28.40
Average (per day).		135.0	23.70	32.0	103.0	...	4.06
Water period. 10 days	9. . . .	76.5	22.87	17.5	59.0	4.89	2.48
	10. . . .	140.9	20.88	29.4	111.5	9.90	4.47
	11. . . .	63.8	29.16	18.6	45.2	6.25	1.55
	12. . . .	169.0	24.30	41.1	127.9	12.52	4.04
	13. . . .	247.5	19.19	47.5	200.0	13.17	4.80
	14. . . .	135.3	22.96	31.1	104.2	9.29	3.33
	15. . . .	192.4	19.58	37.7	154.7	9.88	4.18
	16. . . .	79.2	24.58	19.5	59.7	4.77	1.33
	17. . . .	55.9	27.17	15.2	40.7	3.88	1.48
	18. . . .	173.5	24.91	43.2	130.3	12.25	3.68
	19. . . .	51.5	27.98	14.4	37.1	4.06	1.17
Total.		1385.5	...	315.2	1070.3	90.85	32.51
Average (per day).		138.6	22.73	31.5	107.1	9.09	3.25
Final period. 4 days	20. . . .	67.3	23.60	15.9	51.4	3.88	1.42
	21. . . .	117.8	26.08	30.7	87.1	9.26	2.76
	22. . . .	147.7	23.19	34.3	113.4	9.74	3.46
	23. . . .	145.9	26.49	38.7	106.2	11.34	4.53
	24. . . .	31.2	31.55	9.8	21.4	1.78	0.81
Total.		509.9	...	129.4	380.5	36.0	12.98
Average (per day).		127.5	25.34	32.3	95.2	9.0	3.25

Carbohydrate.—The average daily excretion of carbohydrate dropped from 4.06 grams to 3.25 grams during the water period, and stayed at

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the same value in the final. This is a small difference to be significant but on a uniform diet the evidence is creditable; it points to the same conclusion for moderate water drinking that has been reached up to this time for copious water drinking.

On the basis of these data it appears that the effect of a moderate amount of water with meals is in the same direction as when large amounts are used, although the differences observed are much smaller and not as uniformly found as with the copious amounts of water. Absolutely no harmful results could be detected.

Copious Water Drinking by an Habitual Water Drinker.

The experiment of 14 days, during the 5-day water period of which Subject E took 1333 cc. of water additional with each meal, remains to be considered.

TABLE V.—SUBJECT E.

	Number of stool.	Weight. Grams.	Per cent. dry matter.	Amount dry matter. Grams.	Amount moisture. Grams.	Bacterial dry substance. Grams.	Carbohydrate Grams.
Prel. period. 6 days	1	35.2	28.88	10.2	25.0	2.80	1.02
	2	66.0	28.48	18.8	47.2	6.32	2.03
	3	202.2	24.65	49.8	152.4	15.64	5.59
	4	129.2	24.89	32.2	97.0	9.92	3.17
	5	161.3	21.43	34.6	126.7	10.99	3.73
	6	171.8	22.61	38.8	133.0	11.54	4.43
	7	34.6	27.24	9.4	25.2	3.32	0.97
Total		800.3	...	193.8	606.5	60.52	20.94
Average (per day)		133.4	24.21	32.3	101.1	10.09	3.49
Water period. 5 days	8	90.3	20.15	18.2	72.1	5.83	2.14
	9	37.2	27.33	10.2	27.0	3.33	1.06
	10	249.4	23.57	58.8	190.6	18.61	7.72
	11	74.7	26.57	19.9	54.8	6.01	1.52
	12	258.0	14.81	38.2	219.8	9.86	6.42
	13	52.6	30.23	15.9	36.7	4.81	1.23
Total		762.2	...	161.1	601.1	48.47	20.12
Average (per day)		152.5	21.12	32.2	120.2	9.69	4.02
Final period. 3 days	14	128.3	23.09	29.6	98.7	9.50	3.07
	15	86.4	24.34	21.0	65.4	7.00	1.51
	16	206.5	21.56	44.5	162.0	14.19	3.06
	17	50.6	11.06	5.6	45.0	1.45	0.43
Total		471.8	...	100.8	371.0	32.14	8.07
Average (per day)		157.3	21.36	33.6	123.7	10.72	2.69

Discussion of Data from Subject E, Table V.—An examination of the data in Table V shows that the average amount of feces excreted per day was 133.4 grams during the preliminary period, 152.5 grams during the

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water period, and 157.3 grams in the final period. This marked increase during the water and final periods is not evident from the values for dry matter. During the preliminary period this averaged 32.3 grams per day, during the water period 32.2 grams per day, and during the final 33.6 grams per day, values which are strikingly uniform.

The apparent increase in the average daily amount of feces was thus due to water only, and it would seem that the absorption limit of water in the intestin had been reached. While no difficulty was experienced in drinking the large volume of water, the limit for its absorption had been passed. In the case of Subject W in the first experiment there was no evidence of having reached the absorption limit, while some difficulty was at first experienced in ingesting and disposing of the large quantity of water. This would lead to the conclusion that individuality and dietary habit are important factors.

Carbohydrate.—The average daily excretion of carbohydrate rose from 3.49 in the preliminary period to 4.02 in the water period, and fell to 2.69 in the final period. Stool No. 12 weighing 258 grams contained 6.42 grams of carbohydrate and only 38.2 grams of solid matter; there was pronounced evidence of fermentation. It was passed 15 hours before the usual time and was evidently the result of the intestinal conditions previously mentioned, to which E was subject at times. A larger amount of undigested material than was usual might therefore be expected, and its appearance could not be attributed to the effect of the water. The fall in excreted carbohydrate during the final period is marked, and shows rather conclusively that the high daily average output during the water period was not due to the fact that water interfered with the digestion of ingested carbohydrate but rather that the unusual finding during the water period may logically be explained as above.

Discussion.

The findings of decreased fecal output, both dry matter and moisture, and a decreased elimination of carbohydrate during the periods of water drinking indicate a more complete absorption of both water and dissolved material, with the exceptions noted above. It has been seen, in the preceding papers, that this decreased excretion of solid matter was the result also of a better utilization of the nitrogen (protein) and fat of the diet.

If drinking water with meals brought about a more rapid emptying of the stomach, the carbohydrates might reasonably be expected to give the first evidence of this fact because of all the foodstuffs carbohydrates are normally the first to leave the stomach and a shortening of the time of their sojourn there might mean incomplete hydrolysis of starch by salivary amylase. In experiments on dogs London and Polovzova[6]

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have shown that sucrose and erythrodextrin alone suffer a slight hydrolysis in the stomach, due not to enzymes but to hydrochloric acid, and that under no conditions are carbohydrates absorbed in the stomach. In the duodenum hydrolytic cleavage is very extensive but absorption does not begin until the upper ileum is reached where the greater portion of carbohydrate is absorbed. The great importance of the duodenal juices in carbohydrate digestion is hereby emphasized.

This evidence may be of less value because of the fact that the saliva of the dog has at most but a slight amylolytic power. [6a, 6b, 6c]

In this connection it should also be noted that certain experiments in this laboratory[7] have shown that the production of pancreatic amylase is increased under the influence of water drinking, as would be supposed, and this fact may account in part, for the better utilization of carbohydrate.

As to the absorptive activity of the stomach toward carbohydrates, von Mering[8] concluded from some of his observations that the various sugars could be absorbed in the stomach, absorption being dependent upon the concentration of the solution; that below 5 per cent. glucose was not sensibly absorbed.

The experiments upon the absorption of carbohydrate solutions of different concentrations in the intestin have been very clear in showing the acceleration of absorption by dilution. In experiments on dogs with intestinal fistulas Kaoru Omi[9] has found that in the absorption of solutions of sodium chloride and glucose the percentage of sodium chloride and glucose absorbed depends on the concentration of the solutions introduced and is maximum for isotonic solutions. The absorption of cane sugar is maximum at lower than isotonic concentration. The amount of water absorbed diminishes with increasing concentration of the solute and at slight hypertonicity absorption is checked.

London and Polovzova[10] have made similar experiments with solutions of glucose on dogs with intestinal fistulas and the following are their findings. With increasing concentrations of the glucose solutions introduced, absorption of water in the intestin diminishes progressively. With higher concentrations a diluting secretion begins to flow from the wall of the intestin; its amount runs parallel with increasing concentration of the glucose solution, and at its maximum it may amount to one-half the total quantity of blood in the animal. By this dilution and also by absorption of sugar the concentration of the solution is brought down to 6–8 per cent., a dilution at which absorption takes place very readily in the lower intestinal tract. The secretion of the diluting fluid begins with the coming in of the first glucose solution and continues fairly uniformly. Dilute glucose solutions seem better adapted to absorption than concentrated ones. In the lower portions of the intestinal tract the con-

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centration tends toward a value that is lower than isotonic. The diluting secretion has a small amount of nitrogen (0.1 per cent.) and possesses a kinase, so that in part at least it represents an increased intestinal secretion. For concentrated solutions absorption seems to take place in two stages: in the proximal portion of the intestin the proper dilution is reached, in the distal portion absorption takes place. The intestinal wall differs from the stomach wall in that the latter does not dilute concentrated solutions. The absorption of water and of dissolved substances must be considered as two independent and distinct processes, brought about by different factors. The ability to regulate automatically the concentration of substances to be absorbed is believed to be a part of the function of the digestive juices.

Applying these findings to the experiments on water drinking with meals the explanation for the more complete digestion and absorption of carbohydrates during the period of water ingestion is facilitated. Increased dilution is the effective factor. While it would seem in these experiments that the water taken with a given meal is voided in the urine before the bulk of the food material of that meal has reached the intestin, nevertheless some of the food must be carried along with the water. And further, since absorption is going on more or less continuously in the intestin, the water taken with one meal aids in diluting the products of the previous meal which are in the intestin. Not only is enzyme action more complete in dilute solutions but such solutions are also better adapted to absorption. When the solutions to be absorbed are not dilute the organism must first make them so by pouring out a diluting secretion; if they have been made dilute, the organism is spared this task.

It has been shown by Mosenthal[11] that nitrogen to the amount of about 35 per cent. of the food nitrogen of a mixed diet is daily secreted in the succus entericus of dogs, and that of this quantity an amount equal to 10 per cent. of the food nitrogen is excreted in the feces and an amount equal to 25 per cent. of the food nitrogen is reabsorbed. The metabolic significance of this reabsorption is not understood, but it is probably of great importance. In cases of defective absorption the amount of fecal nitrogen may easily be increased from this source and thus lead to the drawing of wrong conclusions. It is obvious that for various reasons, this possibility need not be considered in connection with water drinking.

That secretion and absorption are exothermic in their nature and require energy has frequently been shown and again recently,[12, 13] and in their first report of observations on the stimulating action of water upon the gastric mucous membrane, Foster and Lambert[14] suggest that a physiological basis for the objection to copious water drinking with meals may be found in the increased activity to which the glands are thus

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forced. If glandular activity requires as much energy as other forms of activity, this special and excessive secretion may be a form of extravagance leading to the weakening and premature death of the cells. In fact, they find that the juice excited by a meal following 5 or 6 hours after a meal with water and its greater demands is less in amount than a normal meal should excite. Whether this is a true gland fatigue, and whether or not such observations point to a premature death of the cells can be determined only by histological examinations.[1] Applying this reasoning to the secretory activity of the intestin a similar form of extravagance may be said to be caused in the intestin by insufficient water ingestion with meals. If there is a loss in energy in the increased flow of gastric juice by water drinking, this is more than compensated by better digestion and absorption of food in the intestin, while the needless energy used in preparing a diluting secretion for food which is too concentrated is a direct loss uncompensated by any subsequent factors making for better utilization of the food. The preservation of the digestive efficiency of the intestin is probably of much greater importance than that of the stomach, since it may be that the main offices of the stomach are not those of a digestive nature.[15]

Conclusions.

(1) It has been shown that in men living on a uniform diet the addition of 1000 cc. of water to each meal causes a decrease in the excretion of fecal material, both dry matter and moisture.

(2) Under the same conditions a decrease in excreted carbohydrate material was also observed.

(3) The better utilization of food material thus evident was not temporary but appeared to extend for some time following the use of water.

(4) The ingestion of a smaller amount of water (500 cc.) and the use of a large volume of water (1333 cc.) by one accustomed to drinking water with meals showed a similar but less marked reduction in the excretion of carbohydrate.

(5) The individual variations noted emphasize the fact that the findings on two or three men possessing different dietary habits and accustomed to ingesting varying volumes of water with meals may not be generalized.

(6) The beneficial effects noted are probably due to the stimulatory action of water upon the digestive secretions, to the increased dilution which facilitates enzyme action and materially aids in absorption, and to a conservation of the intestinal energy involved in the secretion of a diluting fluid which is necessary when insufficient water is ingested.

(7) The average daily output of dry bacterial substance for the 66 stools completely examined was 8.27 grams.

[1] Investigations of this character are contemplated.

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(8) Many desirable and no undesirable effects were obtained by the use of water with meals, and in general, the more water taken the more pronounced were the benefits.

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STUDIES OF THE TRYPTIC DIGESTION OF SILK.[1]

FIRST PAPER.

BY W. S. HUBBARD.

Received September 29, 1911.

Introduction.

Städeler[2] in 1859 first demonstrated that silk was composed of two parts, fibroin and silk glue or sericin. The dissociation products of these parts were, however, first studied by Cramer,[3] who obtained serine from silk glue, and subsequently by Weyl,[4] Vignon,[5] Wetzel[6] and E. Fischer.[7]

Silk fibroin is insoluble in superheated water, dilute acids or alkalies. It has been shown by E. Fischer that fibroin may be heated with water for hours at 117–120°, if the reaction be exactly neutral; however, in the presence of acids or alkalies considerable change takes place under these conditions. According to Weyl it is not attacked by either pepsin or trypsin, a statement disproved with respect to the latter enzyme, by my investigations.

Fibroin contains more than 50 per cent. glycine and alanine and 10 per cent. tyrosine, leucine being present in only small amounts, while

[1] This investigation was undertaken at the suggestion of the late Professor W. F. Koelker, at the University of Wisconsin, and was pursued in its early stages under his direction. The author also wishes to acknowledge his indebtedness to Professor Richard Fischer and Louis Kahlenberg for their interest in the work.

[2] *Ann.*, 111, 12.

[3] *J. prakt. Chem.*, 96, 76 (1865).

[4] *Ber.*, 21, 1407 (1888).

[5] *Compt. rend.*, 115, 613 (1892).

[6] *Z. physiol. Chem.*, 26, 535 (1899).

[7] *Ibid.*, 33, 171 (1902).

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glutaminic and aspartic acids are absent, thus differing materially from other albumins.

The silk glue[1] resembles ordinary gelatin in its solubility, but does not gelatinize so readily and is precipitated by acids. In its chemical composition, however, it differs greatly from gelatin in that glycine is present only in small amounts, if at all, while tyrosine and serine are present in considerable quantity. The following table, based on the results of Fischer and Skita,[2] and Fischer,[3] shows the partial composition of silk fibroin and silk gelatin.

	Glycine.	Alanine.	Valine.	Leucine.	Isoleucine.	Phenylalanine.	Tyrosine.	Serine.	Cystine.	Proline.	Oxyproline.	Aspartic acid.	Glutaminic acid.	Tryptophan.	Arginine.	Lysine.	Histidine.	Total.
Silk fibroin	36.0	21.0	0	1.5	—	1.5	10.5	1.6	..	+	..	+	0	..	1.0	+	+	73.1
Silk gelatin	0.2	5.0	...	..	...		5.0	6.6	..	..	..	..	..	..	+	..	4	..

According to Wetzel,[4] silk gelatin upon hydrolysis yields 1.87 per cent. ammonia and shows a positive reaction for tryptophan.

Since over two-thirds of silk fibroin is composed of only three amino acids, *viz.*, glycine, alanine and tyrosine, it is in this respect the simplest known protein.

Experimental.

The silk used in this investigation was the product technically known as "Winder's Waste," which was purified by repeated digestion with boiling alcohol and final thorough washing with water. Four hundred and eighty grams of this purified material were divided into two equal parts, each of which was placed in a bottle of several liters capacity. Five liters of a 0.2 per cent. sodium carbonate solution and half the extract from three hogs' pancreases were added to each bottle, the solutions being kept aseptic by supersaturating with chloroform. One portion was digested for two months, the other for seven months, a constant temperature of 40° being maintained, the bottles thoroughly shaken several times daily and one gram of Merck's trypsin added to each bottle every two weeks.

At the end of the above-stated periods the filtrate in each case responded to Millon's as well as to the Hopkins-Cole tests. Tyrosine and tryptophan were identified according to the method of Hopkins and Cole.[5] However, it was found impossible to entirely prevent pigmentation or to obtain

[1] *Z. physiol. Chem.*, 34, 481.
[2] *Ibid.*, 33, 151; 35, 23.
[3] *Ibid.*, 37, 508.
[4] *Ibid.*, 29, 386.
[5] *J. Physiol.*, 27, 418.

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an entirely crystallin product, although the dry residue contained numerous crystals throughout an amorphous magma. This residue gave the glyoxylic acid test very positively and quickly. Those products which had been most highly purified by reprecipitation did not give any test for tyrosine. They were moderately soluble in cold water, freely so in boiling water, and on subjecting to dry heat emitted the characteristic skatole-like odors. There can therefore be no doubt that the product contained tryptophan or some compound of tryptophan.

The washings from the first mercuric sulfate precipitate were heated to boiling and hydrogen sulfide passed in until all the mercury was precipitated. The sulfuric acid was removed with barium hydroxide, the excess of barium precipitated with ammonium carbonate, and the solution concentrated to a small bulk, when a precipitate formed. This precipitate on repeated crystallization gave well defined, needle-like crystals, which, however, were still contaminated with a reddish, gummy substance from which it could not be freed even after boiling with charcoal a number of times. That most highly purified product so obtained gave Millon's test very positively, but it, as well as the impure product, gave a negative test for tryptophan.

The filtrate from which the tryptophan and tyrosine had been removed was freed from hydrogen sulfide by passing a current of air through it for several days, and the peptones precipitated out according to the method of Siegfried[1] as follows: The solution was acidulated to the extent of five per cent. with sulfuric acid, saturated with ammonium sulfate, powdered ferric ammonium alum added and the mixture allowed to stand two days. In this precipitation with ferric ammonium alum it was found that the precipitation was much facilitated by keeping the liquid at about 40°. The peptones are contained in the "Eisen niederschlag,"[2] which is dissolved readily and completely in water, the iron and sulfate removed by adding a saturated solution of barium hydroxide and the excess of the latter removed with ammonium carbonate solution. The colorless, neutral solution thus obtained was concentrated to about 10 cc. from a water-bath under diminished pressure at 42°. Absolute alcohol was added to the golden yellow liquid thus obtained, a white gelatinous precipitate resulting, which it was impossible to filter off on account of its tendency to run through the filter. However, upon adding more alcohol small granules began to form in the magma and upon shaking a few times the whole mass became finely granular. This was recrystallized three times in the same way, the total yield of the purified product being less than one gram. It gave a brown ring with the Hopkins-Cole reagent, to Millon's reagent it responded only very slightly, and it gave

[1] *Z. physiol. Chem.*, 35, 164.
[2] *Ibid.*, 38, 289; 35, 164.

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no biuret reaction. This peptone shows a rotation in aqueous solution; $[\alpha]^{D}_{20} = +25.0$. A nitrogen determination by the Kjeldahl method gave 14.71 per cent. of nitrogen compared with 14.94 and 14.96 per cent. for the original silk and 14.88 and 14.89 per cent. for the residual silk after digestion.

Results and Conclusions.

1. It is possible to hydrolyze silk with trypsin.
2. Tyrosine is one of the products of this hydrolysis.
3. Tryptophan or some of its products were isolated from silk for the first time.
4. Tryptic peptones with a dextrorotation were obtained.

ANN ARBOR, MICH.

[FROM THE LABORATORY OF FERTILITY INVESTIGATIONS, BUREAU OF SOILS.]

THE ORIGIN OF CREATININE IN SOILS.[1]

BY M. X. SULLIVAN.

Received September 28, 1911.

Creatinine has been found in soils. Its presence was demonstrated first by Dr. E. C. Shorey,[2] of this laboratory, who extracted it from various soils by means of dilute alkali. Subsequently, as shown in the present paper, it was found in the water and glycerol extracts of planted soils. The creatinine of the soils might have its origin (1) as a result of metabolic activity of microörganisms; (2) from stable manure introduced into the soil; (3) from the disintegration of plant debris and the direct passage from the living plant.

The particular phase of the question of the origin of creatinine in soils, which is considered here, is its presence in plants and consequently in plant debris and the passage of the creatinine into the soil either by the disintegration of the plant debris or as a result of cell sloughing or direct excretion from the living plant.

Creatinine, $C_4H_7ON_3$, is the anhydride of creatine, $C_4H_9O_2N_3$. Creatine is an ever present constituent of muscle and is found in addition in blood and urin. Creatinine is likewise found in muscle, blood and urin, particularly in the urin. The origin of these substances and their physiological relationship within the animal organism have long been under study.

Whatever may be the relationship between creatine and creatinine within the animal, it is certain that one can be converted into the other by appropriate means in the laboratory. Creatine, for example, goes to creatinine on boiling with acids, or, as shown by Folin and Denis,[3]

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[2] *Sci.*, 33, 340 (1910).

[3] *J. Biol. Chem.*, 8, 399 (1910).

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merely by heating crystallin creatine for three hours at a pressure of 4 or 5 kilograms per sq. cm. Creatinine is converted more or less to creatine on warming with alkali.

The literature[1] pertaining to the biochemistry of creatinine and creatine is rather extensive, but will not be reviewed in the present paper which deals only with the presence of creatinine in plants and the medium in which they grow.

Its occurrence in soils had already been reported[2] and will be presented more fully later by Dr. E. C. Shorey, of this laboratory. The effect of creatinine and creatine on plant growth, both of which are beneficial, will be presented by J. J. Skinner, of this laboratory.

Since the chemical properties of creatinine may be found in various text-books of physiological chemistry all that need be said in the present paper is (1) that creatinine is somewhat soluble in cold water and cold alcohol, more so in water and is rather soluble in hot water and hot alcohol, (2) that it is not precipitated by lead acetate, (3) that it gives certain well known color reactions, and (4) forms a characteristic crystallin salt with zinc chloride in neutral solutions.

Though the literature pertaining to the biochemistry of the animal organism is filled with references to creatine and creatinine, the possibility of the occurrence of these substances outside of animal products has not been investigated hitherto to any great extent. Zinno,[3] however, found that cultures of certain bacteria in peptone salt solution gave Weyl's, Salkowski's and Jaffé's reactions for creatinine and he isolated the creatinine as creatinine zinc chloride. Later, Antonoff,[4] relying merely on Weyl's reaction, reported the formation of creatinine by many bacteria in peptone salt solution. More recently Shorey[5] found it in the alkaline extracts of soils.

Previous to the present paper, however, creatinine has never been reported in vegetable matter, although it has been demonstrated often in the flesh of plant-eating animals.

Criteria for Creatinine.

In the present experiments the criteria for creatinine were (1) the color reactions,[6] especially Jaffé's—a red color with picric acid and a few drops

[1] See Magnus Levy, *Van Noorden's Handbuch der Pathologie des Stoffwechsels*, 1, 137 (1906). Hoogenhuyze and Verhloegh, *Z. physiol. Chem.*, 46, 415 (1905). Mellanby, *J. Physiol.*, 36, 447 (1908). Schaffer, *Am. J. Physiol.*, 23, 1 (1908).

[2] E. C. Shorey, *Science*, 33, 340 (1911).

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[4] *Centr. Bakt. Parasitenk.*, 43, 209 (1907).

[5] *Loc. cit.*

[6] In the case of soil or plant extracts, the occurrence of the color reactions is but a presumptive test that creatinine is present, since other substances than creatinine give these reactions. The absence of these color reactions, however, is a sure test

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of sodium hydroxide, a color which is discharged on adding excess of alkali and on acidifying—and Salkowski's—a green color or precipitate of Prussian blue on adding sodium nitroprusside, sodium hydroxide to alkaline reaction and subsequently acidifying with acetic acid and warming; (2) the formation of the characteristic double salt of creatinine and zinc chloride; (3) the regaining of creatinine from the zinc salt by boiling with lead hydroxide with a resulting solution which gave the color reactions.

Creatinine in Planted Soil.

When the concentrated water extracts and water-glycerol extracts of a recently cropped soil were boiled with Fehling's solution, there was more or less reduction of the copper with the formation of a greenish white precipitate. The character of the precipitate suggested the presence of purine bases and creatinine in the soil solution and it became of great interest to determin (1) whether or not the water and glycerol extracts of the cropped soils contained these compounds; (2) whether or not there was a relation between the content of these compounds in the soil and the fact that the crop had grown thereon. As regards the purine bases, it may be said in passing that by appropriate means their presence in the extracts was demonstrated. The main interest, however, was in creatinine for which the water and glycerol extracts of several recently cropped soils were tested.

Arlington Clay Loam.—A sample of Arlington clay loam, upon which cowpeas had been grown for four years, was planted with wheat in paraffin wire pots and the cultures kept in the greenhouse for three weeks. Then the wheat seedlings were cut close to the soil. The samples from the pots were combined and sieved through a one-eighth-inch mesh sieve. For the water extracts, three kilograms of the soil were extracted with six liters of water for twenty-four hours, with frequent stirring, especially in the early stages of extraction. For the glycerol extracts, 3 kilograms of soil were treated with 1200 cc. of pure glycerol, for twelve hours, when 4800 cc. of water were added and the mixture stirred and allowed to stand twelve hours longer. The glycerol itself gave no creatinine test.

The water extract was filtered through paper and 2500 cc. were concentrated to a small bulk. The solution was then made slightly acid with hydrochloric acid and was treated with a large volume of alcohol. After a time a slight precipitate formed. The filtrate, concentrated to about 20 cc., gave Jaffé's and Salkowski's tests for creatinine. The glycerol extracts similarly concentrated to a small bulk gave stronger tests for

that creatinine is absent or present only in traces. When, however, no other substance which gives these reactions is present in a solution, as in the urin, for example, the color reactions are decisive tests for creatinine and the Jaffé reaction has been made good use of as a quantitative test by Folin (*Z. physiol. Chem.*, 41, 223 (1904)) and others.

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creatinine. The concentrated glycerol extract of 2500 cc. of the original solution was syrupy from the glycerol. The syrupy, concentrated glycerol extract was boiled with Fehling's solution and the mixture was filtered. The precipitate was then suspended in water and freed from copper by means of hydrogen sulfide. The filtrate from the copper sulfide was concentrated as far as possible on the steam bath and was still found to contain some glycerol. To the concentrated solution, zinc chloride and sodium acetate were added with the formation of a white precipitate. In twenty-four hours, colorless rosets of creatinine zinc chloride formed.

Dunkirk Clay and Duchess Silt Loam.—In the glycerol extract of a recently cropped sample of Dunkirk clay and in the water and glycerol extracts of a recently cropped sample of Duchess silt loam, creatinine was demonstrated in the same way by means of the double salt of zinc chloride and creatinine.

The creatinine zinc chloride crystals from the Arlington clay loam, the Dunkirk clay and the Duchess silt loam were boiled separately with freshly precipitated lead hydroxide. The filtrates were concentrated to a small bulk. All the concentrated solutions gave Jaffé's and Salkowski's tests. How much of this creatinine, which exists in the concentrated extracts in but small quantities, is present as such in the original extract can not be told, since in the process of concentrating some would be formed from creatine, if present.

Creatinine was also found in the glycerol extract of Arlington clay loam as it came from the field. As judged by the quantity of the double salt of creatinine zinc chloride obtained from the glycerol extracts of Arlington clay loam, planted and unplanted, similarly treated as regards concentrating, precipitating by Fehling's solution, freeing from copper by hydrogen sulfide, concentrating the filtrate from the sulfide and adding zinc chloride and sodium acetate, the extract of the planted soil contained more creatinine than did the extract from the unplanted soil. The increased amount of creatinine in the planted soils must have come (1) from an increased activity of microörganisms on the plant debris and plant constituents and on the organic matter of the soil or (2) directly from the growing plants.

Creatinine in the Water in which Seedlings had Grown.

Since creatinine was found in the extract of soil on which wheat had grown for several weeks, it seemed possible that it might exist in water in which wheat seedlings had grown. Wheat was soaked for about five hours in water and was then placed with a little water in an enameled pan to germinate over night. The seeds with the plumule just showing were then placed on a perforated aluminium disk which was floated on water by means of four air-tight glass tubes. In two days

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the water was changed. The water collected from six pans, about 12 liters in all, was concentrated on the steam bath to 300 cc. To the concentrated solution a few cubic centimeters of concentrated hydrochloric acid and one liter of alcohol were added. In a short time a flocculent precipitate settled out. This precipitate gave a good pentose reaction with orcin and hydrochloric acid, contained phosphoric acid, and gave a slight xanthine test and probably contained nucleic acid. The filtrate from this precipitate was concentrated to about 25 cc. and was then tested for creatinine by means of picric acid and sodium hydroxide. It may be said that many compounds such as levulinic acid, tyrosine, pentose sugars, gallic acid, etc., which might be in the extract of plants, give the red color reaction with picric acid and sodium hydroxide, the red changing to yellow on adding acetic acid, so that this reaction was taken merely as a suggestion that creatinine was present in the water in which the seedlings were growing. The alcohol solution, which gave the color test such as creatinine would give if present, was neutralized and brought to dryness, and was then treated with boiling, absolute alcohol and filtered. The filtrate was again brought to dryness and the process of taking up with absolute alcohol and drying was repeated several times. The final slightly syrupy residue was treated with zinc chloride and sodium acetate in the usual manner and was put in a desiccator. In a few days, stars, radiating clusters of needles, and rosets of creatinine zinc chloride appeared. To make a further test the mass containing the crystals was boiled with freshly prepared lead hydroxide and filtered. The filtrate concentrated to a small volume gave Jaffé's test for creatinine, and also Salkowski's test with the formation of Prussian blue. The original non-acidified solution, when strongly concentrated, likewise gave Salkowski's and Jaffé's tests for creatinine. The amount of creatinine in the water was, however, very small.

Creatinine was likewise found in the water in which the seedlings were growing, with merely the roots in contact with the water.

That most of the creatinine, at times at least, is not present as such in the culture water is shown by the fact that if the water without acidification be concentrated to a small volume in a vacuum, at a temperature between 50° and 60°, Jaffé's test is very slight and at times negative. By warming on the steam bath, especially in the presence of dilute hydrochloric acid, the creatine or other antecedent body is converted to creatinine.

Whether the presence of creatinine or creatine in the medium in which the plants are growing is to be attributed to the action of microorganisms on material sloughed from the roots or to direct osmosis from the intact seed and roots is a question that is rather hard to settle. The following experiment, however, shows that creatinine or creatine may pass from

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seeds by direct osmosis and may pass in the same way through the roots in the normal growth of plants.

Creatinine in the Water in which Seeds had been Soaking.

One kilogram of carefully selected, unbroken wheat seeds, were placed in a flask with two liters of distilled water and the flask was kept in an ice-box at 5–6° for five days. The liquid to the quantity of about 1500 cc. was then poured off the slightly swollen but entirely ungerminated seeds. In the liquid was a medley of organic substances among which a small amount of creatinine was detected by the creatinine zinc chloride method. The creatinine must have come from the ungerminated seeds either as creatinine or as creatine or some other antecedent body which readily changes to creatinine.

Creatinine in Vegetable Material.

Wheat Seedlings.—About five thousand wheat seedlings, nine to eleven days old, were ground and extracted for several hours with boiling alcohol. The hot alcohol was poured off and pressed out of the pulp and allowed to cool. The solution filtered through filter paper was concentrated to a small volume in a vacuum. The concentrated solution was filtered and treated with lead acetate to free it from coloring matter, etc. The fairly colorless filtrate was freed from lead by hydrogen sulfide. The filtrate from the lead sulfide was then concentrated to a small volume. The concentrated solution gave Jaffé's test. Accordingly, zinc chloride and sodium acetate were added to the solution. In the course of several days creatinine zinc chloride appeared in the mass, in the form of stars, crenated hexagonals, needle clusters, and rosets. Treated with lead hydroxide in the customary manner a solution was obtained which gave Jaffé's and Salkowski's tests for creatinine.

Wheat Seeds.—By the creatinine zinc chloride method, creatinine was also demonstrated in the alcohol and water extracts of ground wheat seeds.

Wheat Bran.—In a similar manner, wheat bran was tested for creatinine and on determining its presence a large amount of the bran was used for preparing creatinine zinc chloride. The syrupy mass containing the creatinine zinc chloride was placed on a porous plate and treated with alcohol and water until white. The residue on the plate was dissolved in boiling water and the solution was filtered. The filtrate was brought to dryness on the steam bath in a weighed porcelain dish. To the weighed residue, nitric acid was then added and the solution was brought to dryness and carefully heated in a free flame until the nitric acid was all driven off. The residue was weighed as zinc oxide. The first weighing gave 22.6 per cent. of zinc oxide. On reheating, this was reduced to 21.8, which thereafter remained practically constant. Creatinine zinc chloride requires 22.4 per cent. of ZnO.

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Wheat Straw.—In alcoholic extracts of wheat straw no creatinine could be detected until the concentrated extracts were slightly acidified and boiled. Apparently, creatinine does not exist as such in the wheat straw, while its congener creatine or other antecedent substance does exist therein.

Wheat Protein.—On boiling a water extract of ground wheat seeds a heavy precipitate formed. This precipitate, which gave the protein color reactions, was washed with water, dilute hydrochloric acid, and alcohol until the washings on neutralizing and concentrating gave no tests for creatinine with picric acid and sodium hydroxide. The protein material was then boiled for thirty minutes with 3 per cent. hydrochloric acid. From the filtrate, neutralized and concentrated and taken up with absolute alcohol, a solution was obtained which gave Jaffé's reaction and also crystals of creatinine zinc chloride on treating with zinc chloride and sodium acetate. Since the washings from the protein material also gave creatinine on heating with hydrochloric acid, the protein undoubtedly contained creatine.

Though there is some possibility that creatine and creatinine can be formed from the protein molecule or less complex compounds containing nitrogen, the origin of creatine and creatinine in the plant tissue is still an unsettled question. Whatever the origin of creatinine, it exists in the wheat seed and in the wheat seedlings and is left more or less in the medium in which the seeds have germinated and the seedlings have grown.

Rye, Clover, Alfalfa, Cowpeas and Potatoes.—Creatinine was also found in the alcohol extract of rye, clover and alfalfa seeds, in mature cowpea plants and in potato tubers. The identification in each case was made by the color reactions and the preparation of the characteristic creatinine zinc chloride.

Summary.

Creatinine was found in planted soils as well as in soil which had not been recently cropped, but was present in larger amounts in the recently cropped soil, thus indicating that the appearance of creatinine was connected in some way with plant growth. Creatinine was also found in the water in which wheat seedlings had grown. It was found also in wheat seeds, wheat seedlings, and wheat bran, in rye, clover alfalfa, cowpeas and potatoes. If, as is suggested by several investigators, creatinine in the animal arizes as the result of the breaking up of albumin, then it seems reasonable to expect that creatinine would be found in practically all plants.

Though the amount of creatinine and creatine in vegetable matter is small, it is worthy of attention, since by the decay of plants, green manures, etc., and by direct cell sloughing or even by osmosis, the creatinine and

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creatine are left in water and soil where they exercize an effect on subsequent plant growth. Creatinine seems to persist for a considerable time in soils and may indeed increase in the soil by accumulation. Since both creatine and creatinine have a favorable effect on plant growth, their presence in plants and in the medium in which plants grow has considerable bearing on soil fertility.

WASHINGTON, D. C.

[FROM THE WOODS HOLE LABORATORIES OF THE U. S. BUREAU OF FISHERIES.]

COMPARATIVE PROTEOLYSIS EXPERIMENTS WITH TRYPSIN.

BY GEORGE F. WHITE AND WILLIAM CROZIER.

Received October 20, 1911.

Considerable work has been done on the artificial digestion of various proteins in an attempt to establish their relative values as food. The proteins are digested with either pepsin or trypsin and the rate at which solution takes place is determined. No attempt will be made to review the large amount of literature on this subject, as the present investigation is entirely independent of previous results. These former experiments are of somewhat limited value, as no idea is obtained of the extent to which the soluble products have been hydrolyzed, and the degree of cleavage of the proteins is of great importance, naturally, in a study of comparative digestive properties.

In an article entitled "A Method for Quantitative Determination of Aliphatic Amino Groups," D. D. Van Slyke[1] has described a convenient and generally accurate process by which the amino nitrogen in proteins and their cleavage products can be readily determined. An aqueous solution of the protein is treated with sodium nitrite and glacial acetic acid and the gases evolved passed into alkaline permanganate solution, in which solution nitric oxide is completely absorbed. There is left free nitrogen, which corresponds to the amino nitrogen in the original protein, and the volume of which is measured by passing the gas into a suitable buret. Van Slyke has suggested his method for studying the rate and course of hydrolysis of various proteins by either acids, alkalies, or enzymes, and it is the object of this article to apply it to a study of the comparative digestibility of beef, the edible fish, cod (*Gadus callarias*), and the unutilized dogfish (*Mustelus canis*).

Trypsin was chosen instead of pepsin as the proteolytic enzyme acting on the meats, as the hydrolysis proceeds much farther and a greater insight into the complexity of the end-products of digestion can be obtained.

The meats were boiled with a little water for about fifteen minutes, allowed to drain, and kept ice-cold for analysis and the digestion ex-

[1] *J. Biol. Chem.*, 9, 185 (1911).

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periments. The following table gives results of analyses showing percentage of moisture, and of nitrogen in the dry substance.

TABLE I.

		Cod.	Dogfish.	Beef.
Moisture	(1)	23.10	26.20	43.52
	(2)	23.02	26.10	42.65
Nitrogen	(1)	4.60	6.36	10.54
	(2)	4.62	6.38	10.65

For the proteolysis experiments, enough protein to contain 0.717 gram of nitrogen was weighed out and ground up thoroughly with a little water in a mortar. The sample, together with 0.4 gram trypsin (Merck) and 0.4 gram sodium carbonate, was poured into a 100 cc. measuring flask and made up to the mark with water. After the addition of a little chloroform to prevent putrefaction, the flask was placed in a thermostat kept at a temperature of 36–38.5°. Duplicate analyses were made, and separate mixtures used for the time periods of $^1/_2$, 1, 2, 4, and 8 hours respectively. For analysis, the solutions were rapidly filtered through folded filters, and 10 cc. portions used for total soluble nitrogen by the Kjeldahl process, for the amino nitrogen according to the method of Van Slyke, and for the amino nitrogen after total hydrolysis. The last was carried out by digesting with concentrated hydrochloric acid and removal of this acid after hydrolysis by evaporation on the water bath. The residue was then taken up with a little water, made up to 25 cc. and 10 cc. portions used for the amino determination.

The buret for collecting the nitrogen gas in the amino determination was carefully calibrated and corrections made. Also blank experiments were performed in which no protein was used, but the same quantities of trypsin and other reagents as were used in the proteolysis experiments. Corrections were thus obtained for the total soluble nitrogen and for the amino nitrogen before and after total hydrolysis.

The following tables contain data showing the time of digestion, the soluble and insoluble nitrogen, and the amino nitrogen before and after complete hydrolysis with hydrochloric acid. The figures are the average of duplicate analyses, which showed satisfactory agreement.

In a study of the digestion of protein in the alimentary tract of the dogfish, Van Slyke and White[1] found that there was a large quantity of urea in the intestinal contents, and its source was traced to the gall-bladder. 1.7 per cent. of the bile was urea, or 72.3 per cent. of the total nitrogen was in the urea form. The presence of this urea was mentioned as a possible source of error in the amino determinations of the intestinal matter. These facts suggested testing the dogfish flesh used for the

[1] *J. Biol. Chem.*, 9, 211 (1911).

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TABLE II.—PROTEOLYSIS OF BEEF.

Time in hours.	Sol. N.	Insol. N.	Am. N.	Am. N. after hyd.	Av. size of peptids.	$100 \times \frac{\text{Sol. N.}}{\text{Tot. N.}}$	$100 \times \frac{\text{Am. N.}}{\text{Sol. N.}}$
1/2	0.391	0.326	0.093	0.196	2.11	54.54	23.79
1	0.481	0.236	0.130	0.268	2.06	67.08	27.03[1]
2	0.637	0.080	0.147	0.291	1.98	88.84	23.08[1]
4	0.659	0.058	0.191	0.330	1.73	91.91	28.98
8	0.704	0.013	0.230	0.311	1.54	98.19	32.67

TABLE III.—PROTEOLYSIS OF COD.

1/2	0.613	0.104	0.121	0.293	2.43	85.51	19.73
1	0.683	0.034	0.166	0.319	1.92	95.26	24.31
2	0.715	0.002	0.185	0.303	1.64	99.72	25.87
4	0.716	0.001	0.229	...	..	99.86	31.99
8	0.707	0.000	0.285	0.341	1.20	98.60	40.31

TABLE IV.—PROTEOLYSIS OF DOGFISH.

1/2	0.506	0.211	0.069	0.175	2.54	70.58	14.11
1	0.588	0.129	0.091	0.240	2.05	82.02	15.47
2	0.641	0.076	0.121	0.252	2.08	89.41	18.88
4	0.697	0.020	0.152	0.259	1.71	97.21	21.81
8	0.716	0.001	0.186	0.262	1.42	99.86	25.98

present experiments, for urea. The method of Levene and Meyer[2] for the determination of urea was utilized, and duplicate analyses gave the following: 0.84 per cent. and 0.83 per cent. urea in the boiled dogfish flesh, or 8.27 per cent. of the total nitrogen was in the urea form. This percentage is quite low and should cause little trouble in the amino determination. Any error involved would not affect our later conclusions, which are based on the *low* amino content of the proteolyzed dogfish, while the presence of urea would raise this.

In the seventh and eighth columns of the tables are given the per cent. soluble nitrogen in the total nitrogen, and the per cent. amino nitrogen in the total soluble nitrogen respectively. These results are shown graphically in Figs. 1 and 2. From Fig. 1 it may be noted that conversion of protein to the soluble form takes place very rapidly, and almost entirely in the first 2 hours of digestion, in the case of all the meats. The most rapid hydrolysis, shown by the steepness of the curves, is during the first half hour, while after about 2–4 hours the increase in soluble nitrogen is slow up to 8 hours, when the digestion is practically complete. Of course the trypsin used may not have been a very pure enzyme, but all that was desired in these experiments were relative values, and it may be seen that there are definit differences in behavior of the three proteins. The cod is made soluble the most rapidly of all, while the

[1] Obviously in error.

[2] THIS JOURNAL, 31, 717 (1909).

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dogfish falls intermediate between the cod and the beef. König and Splittgerber[1] found that pepsin digested some boiled fish more readily than boiled beef, which fact agrees with the results above obtained with trypsin. For further literature relating to artificial digestion experiments with fish see Chittenden and Cummins[2] and Popoff.[3]

In Fig. 2, curves are given which show the relationship of the amino nitrogen as determined by Van Slyke's method, and the total soluble nitrogen. This ratio appears to increase slightly with time of digestion, the increase being most apparent with the codfish. This fact will be

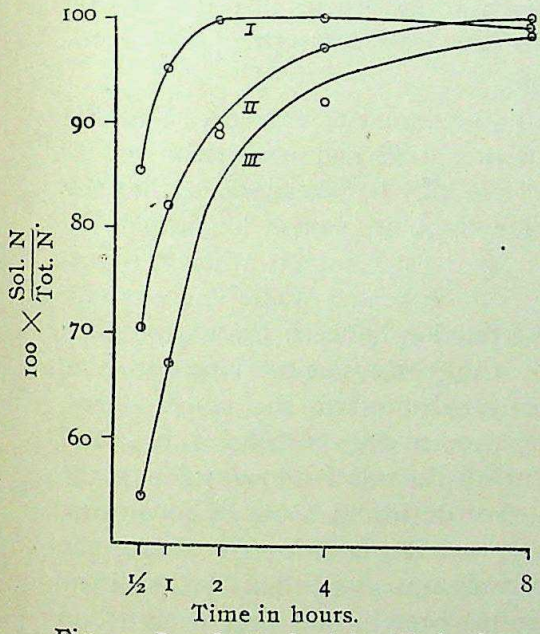

Fig. 1.—I, cod; II, dogfish; III, beef.

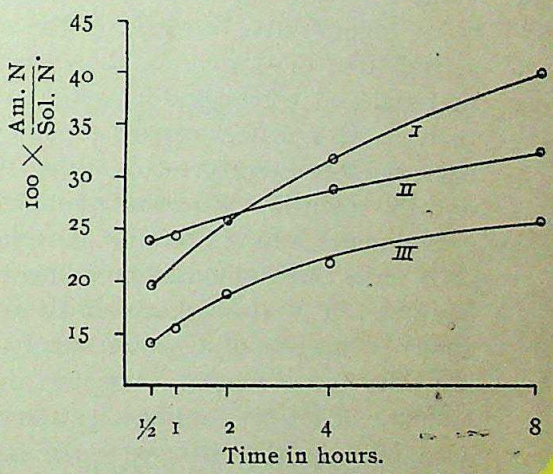

Fig. 2.—I, cod; II, beef; III, dogfish.

referred to later. It may be noted that the ratio is lowest with the dogfish during the whole period of digestion, while the cod, during the first 2 hours having a ratio a little lower than that of the beef, has the highest ratio of all during the remainder of the period.

It is evident then, that while the codfish in tryptic digestion is most readily converted into the soluble form, at the same time the soluble proteins are more easily hydrolyzed than either the beef or the dogfish after an hour or two of digestion, as they furnish more amino nitrogen. The peptides, in other words, are broken down most readily with the cod. Although the beef is least easily made soluble, the hydrolysis of its soluble proteins lies between that of the cod and the dogfish. In columns 8 of the tables of data are given the ratio of the amino nitrogen, obtained by

[1] *Z. wiss. Landwirts.*, 38, 144 (1909).
[2] *Am. Chem. J.*, 65,
[3] *Z. physiol. Chem.*, 14, 584 (1890).

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complete hydrolysis of the soluble proteins, to the amino nitrogen before hydrolysis. This gives approximately the average size of the peptides present in the solution,[1] and the results are in fairly good agreement with the observations regarding the relations between the amino and soluble nitrogen. At the end of the first half hour, the complexity of the peptides in the dogfish solution is 2.54, in the cod 2.43, and in the beef 2.11. With the longest digestion experiments, the average complexity of the peptides decreases to 1.20 in the cod, while the hydrolysis proceeds to 1.54 and 1.42 with the beef and dogfish respectively. This agrees therefore with the figures, for the percentage amino nitrogen, which are in just the reverse order of magnitude. These facts are peculiarly interesting when considered in connection with the following.

It has been suggested recently by various lines of evidence, that the value of a protein to an organism does not depend necessarily on its ready digestibility, but exactly the reverse may be true; that is, that the assimilation of protein in the digestive tract, its conversion into body material and corresponding retention are most complete when the proteolysis has not been carried too far. Van Slyke and White[2] have briefly reviewed the literature concerning the relation between the digestibility and the retention of ingested proteins, at the same time carrying out some experiments which seem to completely substantiate the above views. In a series of metabolism experiments, they fed dogs with boiled beef and various fish meats with a view to establish the relative food value of the latter. The *rate* of digestion was followed during 24 hours by measuring the nitrogen content of the urin drawn at regular intervals, while the amount of nitrogen retained in the organism was measured by the difference between the nitrogen of the ingested protein and that excreted in the urin plus that in the feces.

It was found that the boiled meats varied considerably in their power to maintain nitrogenous equilibrium, and in the rapidity with which they were digested. The important fact was brought out that those proteins that were most readily metabolized caused a negative nitrogen balance; that nitrogen was lost from the organism while they were fed. Those proteins digested slowly brought about a positive retention of nitrogen. Van Slyke and White suggest as causes for loss of nitrogen with rapid digestion, incomplete absorption as shown by the high nitrogen content of the feces; further, as mentioned above, that the organism in absorbing the low cleavage products brought about by rapid and complete hydrolysis, is less capable of building them up into body protein than higher cleavage products. They suggest an optimum rate of digestion for proteins,

[1] *J. Biol. Chem.*, 9, 203 (1911).
[2] *Ibid.*, 9, 219 (1911).

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which shall maintain nitrogenous equilibrium, although this rate may be exceeded as shown by their experiments.

In the above metabolism experiments, of nine meats studied, boiled cod was digested the fastest and was the least capable of maintaining nitrogenous equilibrium. Beef fell approximately in the middle of the series, a little nitrogen being lost during the feeding of it. The following table taken from the above work[1] makes these relations clear, the nitrogen in the urin during the first 9 hours after feeding being a measure of the rate of digestion.

Food.	Boiled cod.	Fried cod.	Boiled beef.	Boiled tautog.	Boiled eel.	Boiled weak-fish.	Boiled mussel.	Boiled salt cod.	Boiled peri-winkle.
N in urin during first 9 hours after feeding.....	1.50	1.36	1.29	1.28	1.24	1.23	1.23	1.07	1.00
N absorbed in 24 hours.....	1.98	1.80	2.58	2.55	1.91	2.53	2.40	2.58	2.57
N excreted in 24 hours.....	2.51	2.48	2.76	2.35	2.20	2.34	2.22	2.29	1.90
N retained.....	—0.53	—0.68	—0.18	+0.20	—0.29	+0.19	+0.18	+0.29	+0.47

The present artificial digestion experiments, it is evident, are in harmony with the metabolism experiments. Boiled cod was found to be digested the fastest of the three meats, at the same time during the greater part of the time of digestion the proportion of low cleavage products was much higher than the other two as shown by the high amino ratio. The dogfish, having only a little greater rate of digestion than the beef, is not broken down as fast as either the beef or the cod. In the light of the metabolism work above quoted and other experiments tending to indicate that too early proteolysis lowers the value of a protein to an organism, it seems safe to conclude that boiled dogfish has a higher food value than cod, and at least as great value as beef. As regards the palatability of dogfish and the economic significance of the above statement, reference may be made to the work of Field.[2]

Summary.

1. The rate and course of hydrolysis by trypsin of the proteins, boiled beef, cod, and dogfish, were studied according to Van Slyke's method. The meats were made soluble at a decreasing rate in the following order: cod, dogfish and beef. The proteolyzed cod solutions gave the greatest amount of amino nitrogen, while the dogfish solutions contained the least. The complexity of the peptides is shown by the ratio of the amino nitrogen after hydrolysis with hydrochloric acid to that present before.

2. The results with the artificial digestion agree with those from metabolism experiments performed on dogs with beef and cod, and indicate

[1] *J. Biol. Chem.*, 9, 226 (1911).

[2] U. S. Bureau of Fisheries Document, No. 622, 44 (1907).

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that dogfish would be digested slowly in the organism and would be capable of maintaining nitrogenous equilibrium—more capable than either beef or cod.

3. There is 0.84 per cent. urea in dogfish flesh, its presence in the blood and bile having been proved by other experimenters.

4. The dogfish, at present considered an unutilized fish, is suggested as a valuable food product.

The authors wish to express their gratitude to Dr. D. D. Van Slyke, of the Rockefeller Institute for Medical Research, for valuable suggestions in the use of his method.

RICHMOND COLLEGE,
RICHMOND, VA.

[CONTRIBUTION FROM THE NEVADA AGRICULTURAL EXPERIMENT STATION.]

MYRISTONE OBTAINED FROM ALFALFA.

BY C. A. JACOBSON.

Received September 6, 1911.

Since alfalfa (or lucern) is now generally recognized as the best, all-round forage crop, being richer in nitrogen, fats and proteins than the ordinary forage crops under cultivation, it seemed of no small consequence to undertake an exhaustive study of its chemical constituents.

The variety of alfalfa employed for the present investigation was the *Medicago sativa* L. which was grown from carefully selected seed and cut in the early blooming period. After curing in the field, the hay was further dried by spreading it out on a granary floor and left for several weeks. When fully air-dried it was ground to a fine meal by passing through a feed mill used only for this purpose.

The alfalfa meal was then put into an extractor of my own construction described elsewhere in this issue, and extracted with hot 95 per cent. alcohol for about seven hours, or until the alcohol came through colorless. The alcoholic extract was then removed from the extractor, heated to boiling on the water bath, and filtered. The filtrate was set aside to cool and then left in the ice box over night, after which the dark green precipitate, which had separated out, was filtered off and dried in the air. The resulting material, which represents 6.8 per cent. of the weight of the dry alfalfa meal, was then extracted with ether in a Soxhlet apparatus until the ether siphoned over clear, which required from 16 to 20 hours. The green ethereal extract from the Soxhlet was poured into a beaker and allowed to evaporate at the room temperature to about one-third of its original volume, when a greenish precipitate had separated out. This precipitate was then filtered and washed several times with ether on a Hirsch funnel connected with the filter pump. The

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light greenish tint on the precipitate could not be washed out with this solvent, but the material itself is slightly soluble in cold ether. This faint greenish substance was dissolved in hot acetone and filtered, after which the solution was allowed to come to the temperature of the room, when the substance separated out as a fluffy voluminous precipitate which was filtered and washed with acetone, dried at first in the air and then in a desiccator over sulfuric acid.

It was first thought that the greenish tint of the material was due to impurity from the chlorophyll residues, but when it persisted after reprecipitating the substance five times from acetone, as well as from absolute alcohol, chloroform and methyl alcohol, retaining its fairly sharp melting point of 76.5°–77° and a constant elementary composition, I concluded that this substance is a single chemical compound of considerable purity. It represents 3.4 per cent. of the green residue before extracting with ether, or only 0.23 per cent. of the dry alfalfa meal. Considerable work has already been done upon this compound, but its discussion will be postponed until some later date.

From 0.5 to 0.8 gram of this material was heated on the water bath, together with about 150 cc. of nitric acid of 1.104 sp. gr., for 12 to 15 hours, or until there was formed a perfectly clear and transparent globule, of a light yellowish color, floating around on the acid solution. Upon cooling slightly, this globule solidified into a cake of waxy appearance, which was washed with hot water until the washings no longer reacted acid. Upon evaporating the nitric acid solution at about 50°, adding water from time to time, monoclinic crystals separated out, which proved to be oxalic acid. The certainty of this is beyond question, since the crystal form, melting point, liberation of carbon monoxide with sulfuric acid, and combustion values were all confirmatory.

By titration with potassium permanganate a quantitative test showed that the weight of oxalic acid formed was 2.8 per cent. of the weight of substance subjected to oxidation, while 97.2 per cent. of the original substance was recovered unoxidized.

The waxy looking cake resulting from the nitric acid oxidation was washed free of acid, pulverized and heated together with about 300 cc. of acetone, which was kept boiling on a water bath for fifteen minutes and then filtered hot. A white insoluble residue was left in the flask, which will be described later. The acetone filtrate was set aside to cool, [illegible] voluminous precipitate settled out. This was reprecipitated [illegible] times from hot acetone, then dried in the air and finally [illegible] sulfuric acid. The substance obtained in this way [illegible] present edition [illegible] color, and a rather indistinct though characteristic valuable fig[illegible]t, beginning to soften at 68° and continuing mo[illegible] At the [illegible]niscus appears on the walls of the melting point tube at 74°,

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[illegible] a small nucleus remain[illegible] melted in the viscid liquid during [illegible] the si[illegible] of the tube [illegible] 75° may pr[illegible] be called its melting point. [illegible] maintain[illegible] lots of [illegible]

By precipitating o[illegible] portions of this material from [illegible] absolute alcohol, methyl alcohol and mixtures by other [illegible] the melting point was not appreciably changed. The substance obtained is undoubtedly myristone, a ketone of the formula ($C_{13}H_{27}$)$_2$CO, identical with the synthetic products obtained by Krafft[1] and Kipping[2]. The latter obtained his product, having a melting point of 76°–77° from myristic acid by heating it with phosphorus anhydride.

Following are the results of combustion on two different lots of myristone from alfalfa, together with Kipping's results on the synthetic product:

	Lot 1.	Lot 2.	Kipping's synthetic $C_{27}H_{54}O$.	Theoretical for $C_{27}H_{54}O$.
C.....	82.11	82.07	81.99	82.14
H.....	13.82	13.60	13.50	13.80

Unsuccessful attempts were made to oxidize this ketone to the corresponding acid by means of chromic-sulfuric acid mixture. The secondary alcohol could be obtained, however, by reducing the ketone with a large excess of sodium in boiling 95 per cent. alcohol. The flask was connected with a reflux condenser, and the solution kept boiling for six hours, after which it was cooled and the precipitate filtered off, washed with water till free of alkali and then precipitated from 75 per cent. alcohol, washed with alcohol of the same strength containing a few drops of HCl, and finally precipitated from acetone. The carbinol thus obtained has a similar melting point to the mother substance, *i. e.*, it begins to soften slightly at 72°, gradually liquefying till a meniscus is formed at approximately 80°, but the unmelted nucleus does not become fully transparent until about 86°. 80°–81° may, however, be called its melting point.

The following table gives the result of combustions on two different lots of this substance.

	Lot 1.	Lot 2.	Kipping's synthetic $C_{27}H_{56}O$.	Theoretical for $C_{27}H_{56}O$.
C.....	81.95	81.80	81.98	81.73
H.....	13.98	14.00	14.09	14.23

From the results obtained it would seem entirely [illegible] that this substance is the secondary alcohol of myristone, which required from ($C_{13}H_{27}$)$_2$CHOH and identical with the dimyristyl carbinol Soxhlet was poured [illegible] from the synthetic ketone. [illegible] temperature to about [illegible] precipitate had separated out. [illegible] several times [illegible] lump. The

[1] *Ber.*, [illegible] 1713.
[2] *J. Chem. Soc.*, 63, 458.
[3] *Ibid.*, 63, 459.

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Cer[illegible] alcohol, having the same p[illegible] exo[illegible] reaction, th[illegible] cocoa le[illegible] slightly [illegible] jects as it proceeds. The [illegible] obtained [illegible] wholly insoluble [illegible] cold alcohol, acet[illegible] constant [illegible] alcohol and petroleum ether, but dissolve [illegible] or less r[illegible] and in ea[illegible] solvents are heated. It is fairly soluble in cold chloroform and [illegible] soluble in cold amyl alcohol. The solubilities of the ketone and its [illegible]rbine do not differ greatly. When one attempts to grind the keton[illegible] a mortar, the particles become strongly electrified and fly out, making a ring of white powder on the table surrounding the mortar.

From the foregoing discussion it would appear that myristo[illegible] is found combined with another substance or substances in the plant structure of alfalfa which can be extracted with hot 95 per cent. [illegible]hol and isolated by weak nitric acid. Work is now in progress on various other substances obtained from alfalfa.

RENO, NEVADA.

NOTE.

An Improved Extractor.—Soon after beginning my alfalfa investigations it became apparent that the ordinary forms of extractor to be had on the market were inadequate for this work.

The alfalfa, being ground to a fine meal or powder, interfered with the siphoning arrangement in the Yocum extractor, which was then the most serviceable, and a new form had to be devized. The results are embodied in this note.

A glass tube 4 feet long and having an internal diameter of $2^1/_2$ inches was drawn out at one end to a diameter of $1^1/_4$ inches, the beginning of the constriction being about three inches from the end, thus making a space of about 2 inches having a uniform diameter of $1^1/_4$ inches and upon which a large rubber stopper is fitted, which in turn is fitted [illegible] the mouth of the distilling flask as shown in the figure. Another [illegible] tube $3^1/_2$ feet long having an internal diameter of 2 inches is grou[illegible] one end to fit into the small glass adapter also represented in the figure. The other end is flared and serrated so that it will just go into the large tube. The glass adapter is conical in shape, ha[illegible] an opening of only $^1/_4$ inc[illegible] at the lower end and provided with three gla[illegible]s fused to the [illegible] which serve to support the adapter and inside tube [illegible] constriction of the outside tube, and still leaving space

The [illegible]ness [illegible] this work appea[illegible] 198.
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[illegible] a small nucleus remaining [illegible] melted [illegible] indefatigable inquirer, [illegible] ring elain [illegible] the si[illegible] of the tube [illegible] significance which [illegible] call d it, whic[illegible] is co[illegible] maintan[illegible] lots of [illegible] e in the indu[illegible]

After the inside tu[illegible]es of this [illegible] have been [illegible] olute the substance to be extracted, they [illegible] by oth[illegible] the outside tube was while in a horizontal position and then co[illegible] obted with the distilling flask and clamped. Into the upper end of the outside tube is fitted a bulbed reflux condenser. When the solvent is brought to boiling on the water bath, the vapors pass up between the walls of the two glass tubes, and after being condensed drop on the material in the inside tube, saturating it, and are then returned to the distilling flask from the lower end of the adapter.

[illegible] special advantages of this form of extractor or percolator are: The large capa[illegible] coupled with its simplicity and cheapness of construction, the convenience of emptying and refilling, together with the fact that the material is extracted at practically the temperature of the vapor of the solvent. Only one liter of solvent is required to extract more than two liters of material. When used in extracting fine alfalfa meal with alcohol, four or five hours are required before the extraction is complete.

The extractor has been in almost daily use for over a year, with entire satisfaction. If the outside glass tube is clamped too tightly it may break when the hot vapors come in contact with it. This difficulty is obviated by using a copper tube of the same dimensions. It was found advantageous to surround the outside tube with a strip of felt cloth in order to conserve the heat during extraction. C. A. JACOBSON.

RENO, NEVADA.

NEW BOOKS.

Chemistry, an Elementary Textbook. By WILLIAM CONGER MORGAN [illegible]ND JAMES A. [illegible]YMAN. The MacMillan Co., New York. Pp. xiv + 429. Price, $1.2[illegible] net.

[illegible]e ideal of the authors of this book is that "the student shou[illegible] never [illegible]d to get the idea that chemistry is a science that dwells insi[illegible] of laboratories and acts chiefly in beakers and test-tubes. He should be conscious continually of its presence about him on every hand, in nature, in the home, and in the whirring world of industry." They "have tried to bring out the [illegible]stic side of the science." In following these ideals the mistake has not been made of presenting chemis[illegible]tive science only. Much pains is taken to give in a clear a[illegible] the underlying theories and principles of our science was poured [illegible] reversible reactions and quest[illegible]ature to about [illegible] elementary textbook. [illegible] had separa-

[illegible] the authors fo[illegible]mber of oth[illegible]r authors in[illegible]l times [illegible]ons as "spo[illegible]eou[illegible] and endothermic re[illegible] The

[illegible] J. Ch. Soc., [illegible]
[illegible] Ibid., 65, 429.

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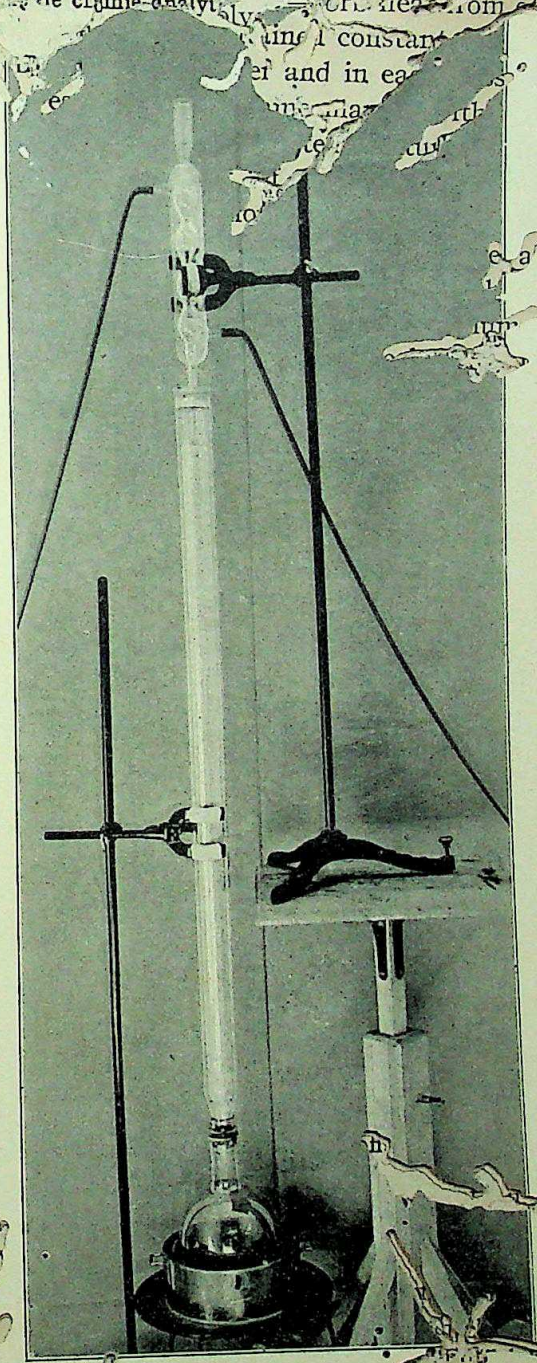

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[illegible] BRACHER, M. **Anleitung zur Erkennung und Prüf[illegible]** exo[illegible]mic reaction, th[illegible] reac[illegible] 1. [illegible] pp., 87 in: [illegible], 615 pp., 6.60 [illegible] slightly [illegible] jects as it proceeds, whe[illegible] H [illegible] **de chimie analy[illegible]** [illegible] from other substances. So long as t[illegible] are is maintained constant [illegible] class o[illegible] reactions is just as "spo[illegible]" as the other and in each class the speed of the reaction changes in essentially the same manner with the concentration of the reacting substances and with the temperature.

In the statement on p. 80 that "if an insoluble substance is formed equilibrium is impossible" the authors seem to have overlooked the fact that electrolytes are probably never wholly insoluble and that while the equilibrium is displaced very far to one side in the precipitation of difficultly soluble salts, there is still a true equilibrium which is [illegible] important in considering problems of analytic[illegible]try. However, the statement of the text is possibly justified from a pedagogical standpoint in a text to be used in high schools and by Freshmen.

The book is well illustrated. A considerable number of half-tones from photographs of natural objects and of portraits add to the human interest and the inclusion of several pictures from the Pacific Coast adds to the value of the book for Western students and does not hurt it any for others.

W. A. N.

Traité de chimie générale. Par W. NERNST. Ouvrage Traduit sur la 6e Édition Allemande, par A. CORVISY. Première Partie: Propriétés Générales des Corps; Atome et Molécule. 510 pp. Paris: Libraire Scientifique A. Hermann et Fils. 1911. Prix, 12 francs.

This book is a translation of the first half of Nernst's *Theoretische Chemie vom Standpunkte der Avogadro'schen Regel und der Thermodynamik*, familiar to all students of chemistry, either in the original or in the English translation. The sixth German edition, which was published in 1909, differs from the earlier editions, notably in the addition of chapters on radioactivity and on the atomic theory of electricity, and in important additions to the chapter on the colloidal state, bringing these sub[illegible] down to date. Any comment on the book itself, already re[illegible] in its earlier editions in THIS JOURNAL, is unnecessary, save to add that the additions increase the value of the book as a text-book for advanced students and for reference.

JAS. LEWIS HOWE.

Grundriss der Kolloidchemie. By WO. OSTWALD, Priv[illegible] der Universität Leip[illegible] [illegible]llig umgearbeitete und wesentl[illegible]vermehrte Auflage. Erste [illegible] Theodor Steinkopff. 329 pp.

The [illegible]ness of the period which has elapsed since the first edition of this work appea[illegible] is indicative of the esteem in which it is he[illegible] The present edition is much enlarged and amplified in every way, and [illegible] valuable figures have been added.

At the present time, when the vast field of colloid ch[illegible]stry is [illegible]

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beginning to yield [illegible] indefatigable inquirer, [illegible] we can dimly foresee [illegible] significance which [illegible] knowledge may come to have in [illegible] dangerous [illegible] in the industry of medicine, the appearance of a compendium of this character containing an impartial statement of a wide range of facts and [illegible] hypotheses which have been erected upon them is singularly opportune. This book should unquestionably find a place upon the library shelves of every chemical or biological laboratory, whether devoted primarily to the investigation of industrial problems, or to the investigation of problems of medicine or of "pure" science. Other works, which are now appearing with frequency, aim at surveying relatively restricted portions of this great [illegible] The present work embraces the entire field and is of as much interest to the [illegible] chemist as to the protein chemist, to the medical chemist as to the physical chemist.

The literature references are very exhaustive and form not the least valuable portion of the book. The paper and print are excellent and both the author and the publisher are to be congratulated upon the neat and workmanlike arrangement and appearance of the book. A second part is promised which will contain, among other chapters, a discussion of the optical and electrical properties of colloidal systems and a description of the experimental methods of colloid chemistry.

T. BRAILSFORD ROBERTSON.

Einführung in die Kolloidchemie. Third edition. BY PROF. VIKTOR POSCHL. Dresden: Steinkopff. 80 pp. Price, 2 Marks.

This is a simple treatment of colloids and contains the most condensed information, in systematic arrangement, of any of the briefer works on the subject. It includes a good list of references and title and author indexes.

W. R. WHITNEY.

Die Bedeutung der Kolloide fuer die Technik. BY KURT ARNDT. Dresden: Steinkopff. 46 pp. Price, $1^1/_2$ Marks.

This is a second edition of the pamphlet of two years ago. It is a very valuable adjunct to Poschl's book (previous review), as it deals with applications of principles there described. For example, the colloidal state is considered in connection with glass, minerals, ceramics, cements, dyes, soaps, tanning, brewing, etc. Absorption, electro-osmosis and other colloid phenomena are also discussed from a technical standpoint.

W. R. WHITNEY.

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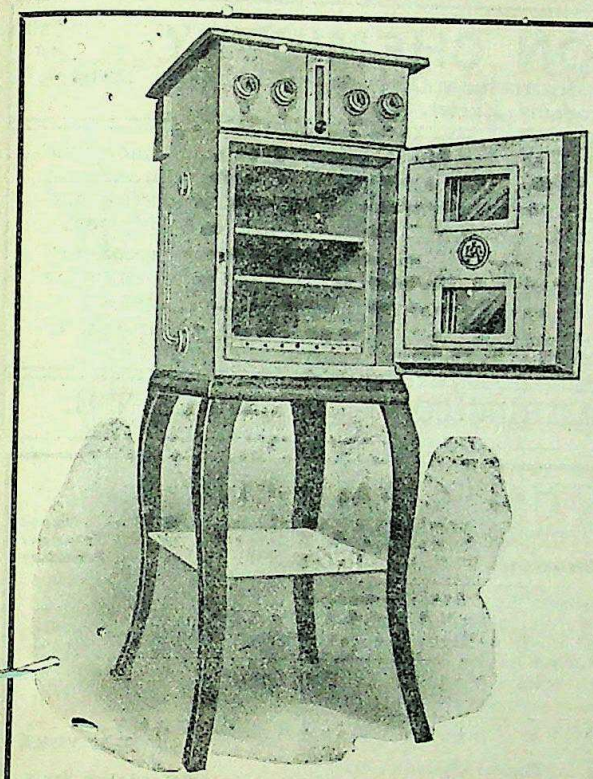

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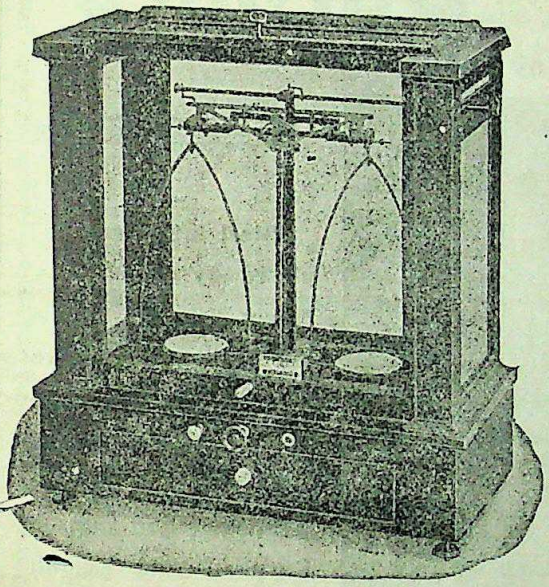

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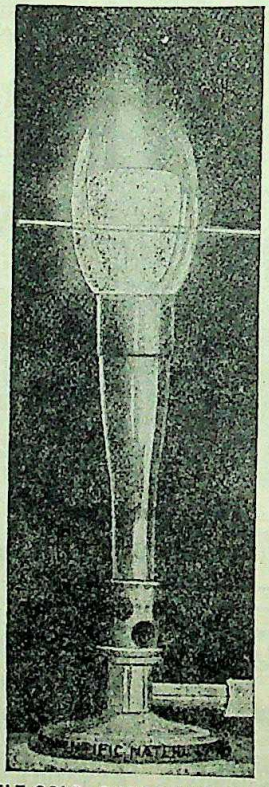

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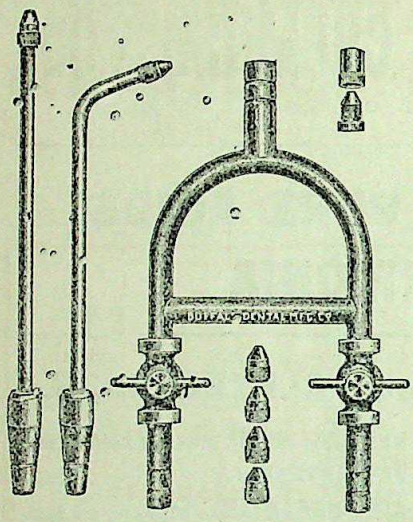

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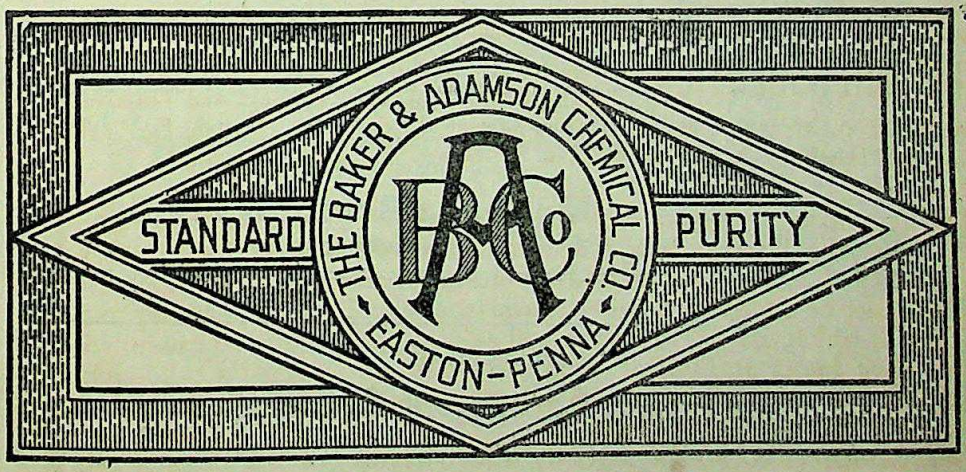

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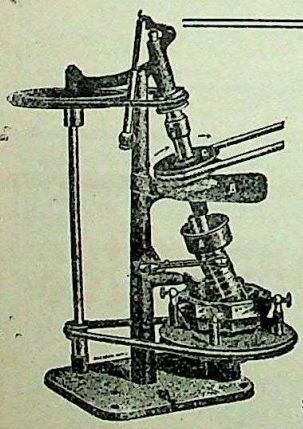

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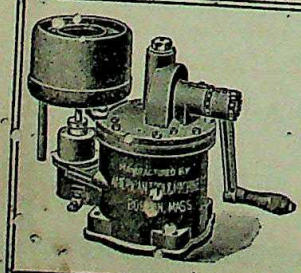

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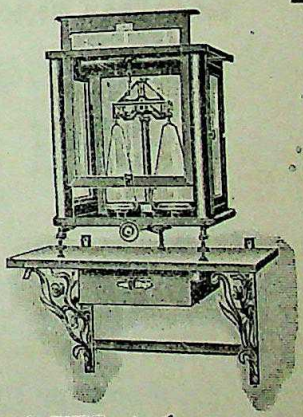

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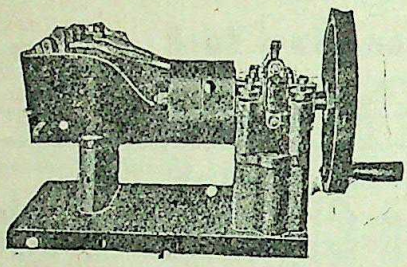

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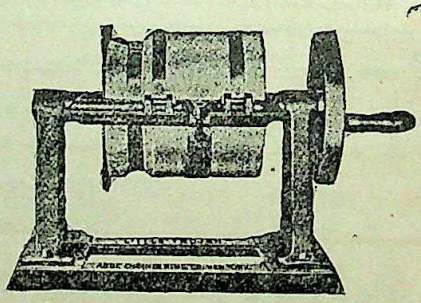

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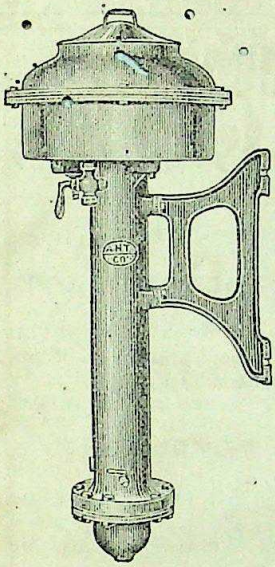

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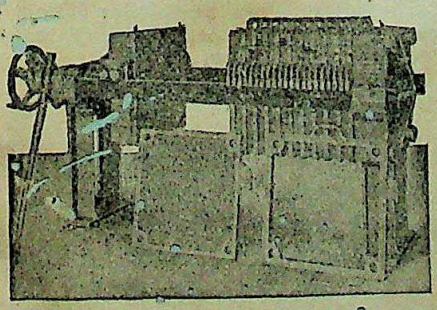

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